Iridium Complexes of some Main Group Halides

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To my parents

CONTENTS

Abstract

This thesis describes the preparation and structure of some main group halide complexes of iridium. The reactions between trans-$[Ir(CO)Cl(PEt_3)_2]$ and the following have been investigated: BCl_3, PCl_5, PCl_3O, PCl_2F_3, $PClF_4$, PF_4H, PMe_2Cl, $AsCl_3$, SCl_2, S_2Cl_2, SPhCl, $SOCl_2$, SO_2Cl_2, $SeOCl_2$, Se_2Cl_2, SePhCl and Cl_2. In most cases, reaction appears to proceed through oxidative addition, though this may be followed by loss of halide ion from the product.

The reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ with HCl, Cl_2, PF_5 and XeF_2 are described, the last giving $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ whose reactions with H_2O and PF_5 are included. The compound $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ reacts with BCl_3, B_2H_6, N_2O_4, Se_8, H_2Se, HCl/BCl_3, XeF_2, PCl_5 and Cl_2, and the products of these reactions as well as the reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ are discussed.

All the complexes described here have been studied by multinuclear n.m.r. spectroscopy and in some cases their infra-red spectra and partial elemental analyses have been obtained. The X-ray crystal structures of seven of the products are also given.

Abbreviations

Ac	= acetyl, CH_3CO
Bu	= butyl superscript n,i,s or t normal, iso, secondary or tertiary butyl
cod	= η^4-1,5-cyclooctadiene
cp	= η-5-cyclopentadienyl
cy	= cyclohexyl
dbu	= 1,8-diazabicyclo[5.4.0]undec-7-ene
dme	= 1,2-dimethoxyethane
dmpe	= 1,2-bis(dimethylphosphino)ethane
FAB	= Fast Atom Bombardment
H_2dmg	= dimethylglyoxime
Me	= $-CH_3$ (methyl)
nbd	= η-4-bicyclo[2.2.1]hepta-2,5-diene
n.m.r.	= nuclear magnetic resonance
OAc	= acetate anion CH_3COO
p-cymene	= η-6-$MeC_6H_4CHMe_2$-p
Ph	= $-C_6H_5$ (phenyl)
phen	= 1,10-phenanthroline
p.p.m.	= parts per million
Pr	= propyl
py	= pyridine
R	= alkyl, unless otherwise specified
thf	= tetrahydrofuran
XPS	= X-ray photoelectron spectroscopy

Chapter 1

Introduction

This chapter provides a brief account of the chemistry relevant to this thesis.

1.1 Oxidative Addition Reactions

An oxidative addition reaction occurs when a compound behaves simultaneously as a Lewis acid and Lewis base [1-6] and is written in general:

$$L_yM^n + XY \longrightarrow L_yM^{n+2}(X)(Y).$$

The reverse reaction is called reductive elimination. Vacant co-ordination sites are required on the initial L_yM^n compound and there must be non-bonding electron density on the element M^n, as well as oxidation states separated by two units. When molecules such as H_2, HCl or Cl_2 add, two new bonds are made to the central element and the H-H, H-Cl or Cl-Cl bond is broken. There are many mechanisms suggested for oxidative addition and they are discussed in Section 1.2. Some examples of this type of reaction are:

$$SF_4 + ClF \xrightarrow{CsF} SClF_5 \qquad (7)$$

$$PF_3 + Cl_2 \longrightarrow PCl_2F_3 \qquad (8)$$

$$SiF_2 + H_2S \longrightarrow SiF_2H(SH) \qquad (9)$$

Metal complexes also undergo this type of reaction, often when a square planar d^8 complex is converted to an octahedral d^6 complex by the addition of a covalent molecule to the co-ordination sphere. Oxidative addition to a sixteen electron system will produce an eighteen electron system. An example of this is the addition of hydrogenchloride to carbonylchlorobis-(triphenylphosphine)iridium(I) (Vaska's complex).

$$[Ir(CO)Cl(PPh_3)_2] + HCl \rightleftharpoons [Ir(CO)Cl_2H(PPh_3)_2]$$

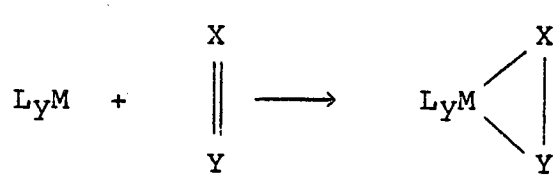
The position of the equilibrium may lie on the reduced or oxidised side and depends on two factors:

(a) The metal; most importantly the energy required for the oxidation. The high oxidation states of the heavier metals of any triad are more stable states than those of the lighter metals, so iridium(III) is more stable than rhodium(III). The equilibrium reaction given above lies further to the right for iridium than for rhodium.

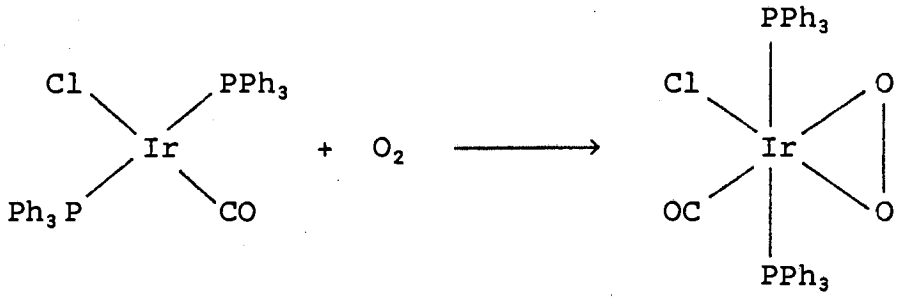
(b) The molecule XY; here the bond energy of XY is important as are the MX and MY bond energies. Considering the thermodynamics only, low XY and high MX and MY bond energies favour oxidation, high XY and low MX and MY favour reduction.

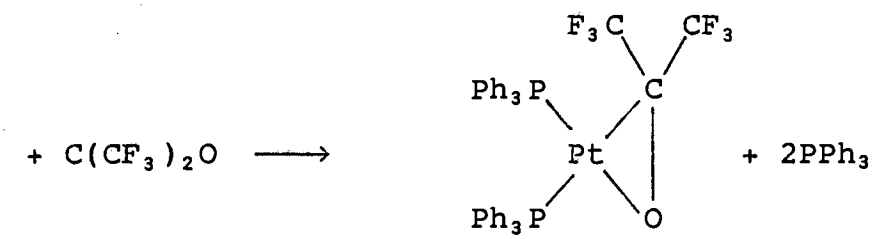
Comparing the stabilities of different complexes, the higher oxidation states will be stabilised by ligands which are more electron-donating. For example if the phosphines in Vaska's compound are replaced by more basic phosphines, the iridium(I) complex is more readily oxidised.

Molecules containing multiple bonds may be added oxidatively without cleavage of the molecule to obtain complexes with three membered rings, for example:



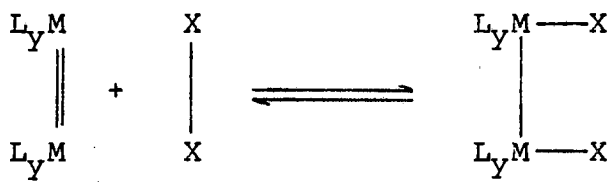
Some specific examples are dioxygen and $C(CF_3)_2O$:





There is some speculation concerning the nature of the reaction with dioxygen [10].

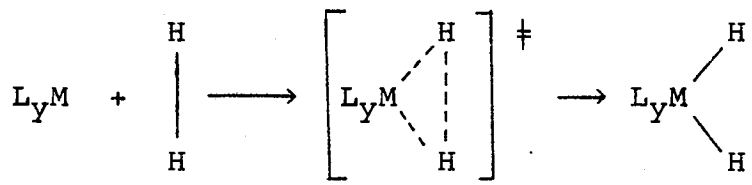
Although rare, reactions of the type:



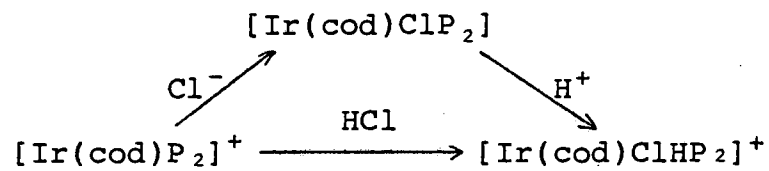
are usually referred to as oxidative addition / reductive elimination reactions [11].

1.2 Stereochemistry and Mechanism of Addition

When a molecule XY adds without severance of X from Y, the addition is necessarily cis. When X and Y separate, the product may be one or more of several isomers with cis or trans X and Y. Kinetic studies of dihydrogen addition to Vaska's compound indicate cis addition via a non-polar transition state [12].



The addition of HCl and HBr to Vaska's compound forms cis or trans mixtures depending on the solvent and on the dryness of the solvent [13,14]. In polar media, initial protonation would produce a cationic five-co-ordinated intermediate which could isomerise by the Berry mechanism. However it may be that the halide ion adds first rather than the proton [15,16]:

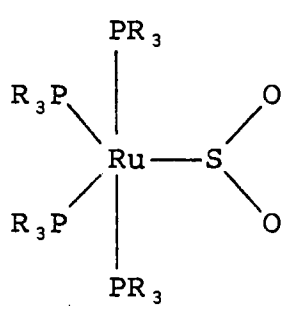


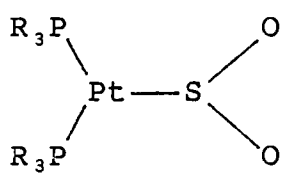
The compound $[Ir(cod)P_2]^+$ does not react with H^+ (P = $PMePh_2$).

Some alkyl halides oxidatively add by an S_N2 mechanism [6]; for example methyl iodide adds to Vaska's compound in this way. However the majority of alkyl bromides and chlorides react with iridium(I) complexes by a free radical mechanism [17,18].

1.3 Donor Adduct Formation

Donor adduct formation occurs when a molecule adds to a metal complex but does not oxidise the metal [2]. A wide variety of donor adduct complexes have been formed with sulphur dioxide [19]:





The formation of these compounds depends on two factors:

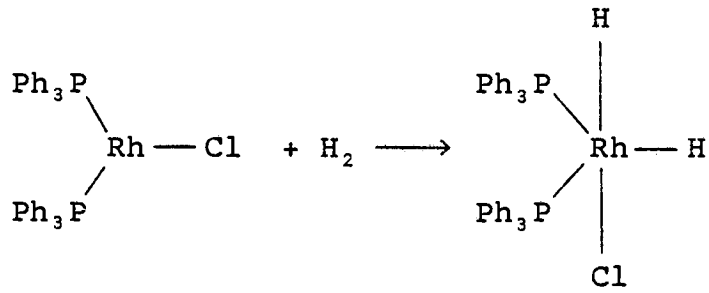
(a) Electron donation from filled molecular orbitals on the ligand to unfilled orbitals on the metal.

(b) Metal-to-ligand donation of electron density from the d orbitals of the metal to the unfilled p or pi orbitals on the ligand.

High metal-to-ligand donation might be expected for a strong Lewis acid adduct and this has been shown for the adduct formed between Vaska's compound and borontrifluoride [2,20]. When more basic phosphines are used to replace the triphenylphosphines, the adducts have greater association constants than those of Vaska's compound [21].

1.4 Homogeneous Catalysis

The extensive studies of oxidative addition reactions have largely resulted from the need to understand the mechanisms of the reactions of homogeneous catalysts. Amongst the many such catalysts the d^8 metal complexes are important [1,3,4,5,22]. Chlorotris-(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) catalyses the hydrogenation of alkenes under mild conditions [23] and carbonylhydridotris(triphenylphosphine)-rhodium(I) catalyses the hydroformylation of alkenes [24]. The catalytic cycles of these compounds contain a step involving oxidative addition of dihydrogen; for example the following is part of the Wilkinson's catalyst cycle.



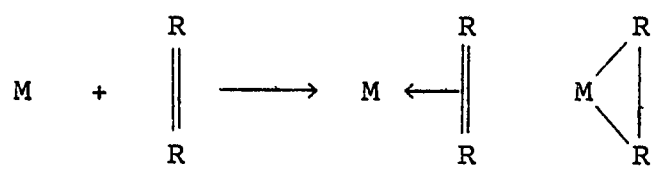
1.5 Oxidative Addition: An Alternative View

The term "oxidative addition" has been recently discussed [25]. Some problems with its use are pointed out and these arise from two sources:

(a) Inability to define the formal oxidation state of a complex in all cases.

(b) Existence of "oxidative addition" reactions that are not oxidative.

The addition of ethylene to a metal (R = CH_2):



(A) (B)

can be described as ligand addition (A) or oxidative addition (B) depending on the nature of the product. For ethylene structure A is more appropriate, but for tetrafluoroethylene (R = CF_2) structure B is a better model.

In ^{13}C n.m.r. studies of some "oxidative addition" reactions of iridium complexes it was shown that the electron density on the metal increased in some cases [26,27]. For example

$$[Ir(cod)_2]^+ + H_2 \longrightarrow [Ir(cod)_2H_2]^+$$

had an oxidation state change of approximately -1. Studies by Louw et al [28] using XPS to obtain an oxidation state for the metal have shown that only in a few cases is there an oxidation state change of +2. Using a standard of +3 for the oxidation state of $[Ir(phen)(cod)Cl_2]^+$, the following oxidation states were obtained for complexes of $[Ir(phen)(cod)]^+$ with some small molecules:

Molecule	Oxidation State
C_2H_2	1.00
C_2H_4	1.11
O_2	1.53
CH_3I	2.58
HCl	3.00

We must remember that "oxidative addition" is based on the formal definition of oxidation states and take due care when considering such reactions.

1.6 Reactions of Main Group Halides with $[Ir(CO)Cl(PR_3)_2]$

The preparation of $[Ir(CO)Cl(PPh_3)_2]$ was first reported in 1962 [29] and the reactions with HCl [29], Cl_2 [29] and $HgCl_2$ [30] were soon noted. The structures of the HCl [2,31,32], hydrogenhalide [13,14,33] and $HgCl_2$ [30] addition products have been investigated by infra-red spectroscopy and a crystal structure of $[Ir(CO)Cl_2(HgCl)(PPh_3)_2]$ was determined [34]. Both cis- and trans- addition products are formed in the above reactions, depending on the reaction conditions, which may be because of halide exchange before the reaction, or halide exchange in the products [13,35].

We shall now consider some of the reactions of

Vaska's compound and its phosphine analogues.

1.6(a) Boron [36]

Adducts of the type $[Rh(BX_3)(CO)XL_2]$ (X=Br,Cl;L=PPh_3,$AsPh_3$) are formed from reactions of BCl_3 and BBr_3 with $[Rh(CO)XL_2]$. The BBr_3 adducts are more stable than the BCl_3 adducts. Spectroscopic data indicate that Rh-B dative bonds exist in these compounds [37,38].

The reaction of $[Ir(CO)ClL_2]$ with BF_3 shows that mono- and bis-BF_3 adducts are formed when L=PPh_3 or P(p-biphenyl)$_3$, but only mono adducts when L=PEt_3 or $PMePh_2$ [20,21]. The adduct $[Ir(BF_3)(CO)Cl(PPh_3)_2]$ disproportionates into $[Ir(BF_3)_2(CO)Cl(PPh_3)_2]$ and $[Ir(CO)Cl(PPh_3)_2]$ upon removal of solvent.

1.6(b) Silicon, Germanium and Tin [39]

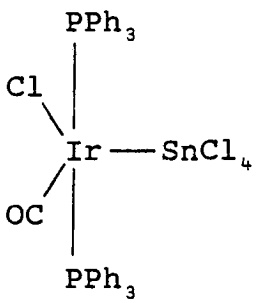
1.6(b)(i) Silicon [40] and Germanium

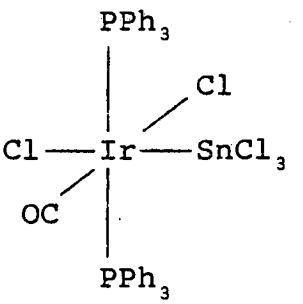
Reactions of $SiCl_3H$ [41], $SiMeCl_2H$ [41] and MH_3X (M=Si,Ge, X=H,Cl,I) [42,43] with $[Rh(CO)Y(PEt_3)_2]$ (Y=Cl,I) show that oxidative addition occurs across the Si-H bond. The redox equilibrium is very sensitive to the group X and a number of the products dissociate at room temperature.

Extensive studies have been made into the reactions of MH_3Q (M=Si,Ge, Q=H,Cl,Br,I) with Vaska's compound [44] and its triethylphosphine analogue [45]. Most of these, as well as the reaction between Vaska's compound and $GeMe_3H$ [46], show oxidative addition across an M-H bond. Addition of the Si-Si bond of Si_2Cl_6 has also been reported [47].

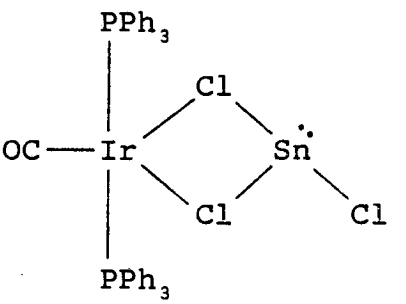
1.6(b)(ii) Tin

Reaction of $SnCl_4$ with Vaska's compound gives two products which may be the donor adduct or the oxidative addition species [31,48,49]:





The reaction of $SnCl_2$ with Vaska's compound produces the species [49]:



1.6(c) Nitrogen and Phosphorus

1.6(c)(i) Nitrogen

The reactions of Vaska's compound with OClN and SClN are oxidative additions across the N-Cl bond [50].

1.6(c)(ii) Phosphorus

The compounds PXF_2S (X=Cl,Br) and $PBrF_2O$ have been shown to add oxidatively across the P-Cl and P-Br bonds to Vaska's compound [51].

Reactions between $[Ir(CO)X(PEt_3)_2]$ and PF_2Q (X=Cl,Br,I, Q=H,Cl,Br,I) proceed via a five-co-ordinated complex of iridium(I) to a six-co-ordinated iridium(III)

complex [52-54]. The reaction of the same metal complex with phosphorustrichloride was also oxidative addition [53,55,56]. Corresponding reactions of the rhodium analogue of the latter metal complex have also been carried out, but the rhodium(III) octahedral complexes obtained were not as stable as the iridium complexes.

1.6(d) Sulphur and Selenium

Despite some extensive work in this area, the reviews consider metal $-SO_2$ [19], $-SR_2$ [57] and $-EX_n$ [58] complexes (E=S,Se,Te, X=halide).

Much work has been done on the reactions of $SRClO_2$ with $[Ir(CO)Cl(PR_3)_2]$, which are examples of oxidative addition across the S-Cl bond [59-62]. The compounds are studied by infra-red techniques, as are the products of the reactions between Vaska's compound and SRClO [63], SClO(OR) [63], SCl_2O [64-65] and SCl_2 [66]. All these were oxidative additions across the S-Cl bond. Similarly, the reactions of SRCl [3] and S_2Cl_2 [66] are reported as oxidative addition reactions although no experimental details are given. The oxidative addition of $S_2(C_6F_5)Cl$ to Vaska's compound was also investigated [67]. Reaction of $SClF_5$ produced $[Ir(CO)Cl_2F(PPh_3)_2]$ [68].

There are no reports of the addition of selenium halides to Vaska's compound, but selenols and H_2Se have oxidatively added [69], as has H_2S [70].

1.6(e) Dichlorine

Oxidative addition of dichlorine to $[Ir(CO)Cl(PR_3)_2]$ complexes has been well studied [29,71,72] and a crystal structure of trans-$[Ir(CO)Cl_3(PPh_3)_2]$ has been reported [73].

1.7 Transition Metal Complexes of Three-co-ordinated Phosphorus, Arsenic, Antimony and Bismuth

The synthetic routes to such compounds are varied, and we shall attempt to cover these together with some examination of the reactivity of these complexes.

1.7(a) Synthesis

1.7(a)(i) Dimers

A number of workers have used the reactions of two dimers to produce three-co-ordinated complexes. Reaction of $[\{As(C_6F_5)_2\}_2]$ with $[\{M(CO)_ncp\}_2]$ is as follows (M=Fe,n=2, M=Mo,n=3)[74] :

$$[\{As(C_6F_5)_2\}_2] + [\{Fe(CO)_2cp\}_2] \longrightarrow 2[Fe\{As(C_6F_5)_2\}(CO)_2cp]$$

Similarly, the reactions of tetrakis(trifluoromethyl)-diphosphine [75] and -diarsine [76] with binuclear metal complexes result in the formation of three-co-ordinated phosphorus and arsenic:

$$[\{E(CF_3)_2\}_2] + [\{M(CO)_ncp\}_2] \longrightarrow 2[M\{E(CF_3)_2\}(CO)_ncp]$$

(E=P,M=Fe,n=2; E=As,M=Fe,n=2,M=Mo,n=3).

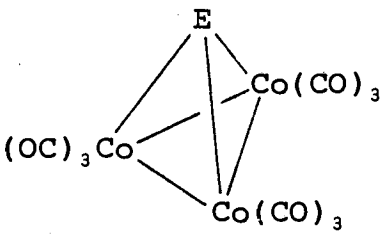
Other species are formed by the reaction of ECl_3 (E=As,Sb) with $[\{Fe(CO)_2cp\}_2]$ [77,78]:

$$ECl_3 + \tfrac{1}{2}[\{Fe(CO)_2cp\}_2] \longrightarrow [Fe(ECl_2)(CO)_2cp][ECl_4]$$

Neutral species $[Fe(EX_2)(CO)_2cp]$ were also obtained by the

same workers (E=As,X=Cl,Br; E=Sb,X=I; E=Bi,X=Cl).

Reaction of $[Co_2(CO)_8]$ with AsI_3 [79] or with P_4 or PX_3 (X=Cl,Br,I) [80] leads to unstable complexes of the form:



E=P,As

The following reaction is also of this class [81].

$$[C_5H_{10}N]_2[P\{PO(OEt)_2\}_2] + W(CO)_6 \xrightarrow{-CO} [C_5H_{10}N]_2[W(CO)_5\{P[PO(OEt)_2]_2\}]$$

1.7(a)(ii) Elimination of Covalent Chlorides

Schrauzer et al [82] have produced $-EPh_2$ ligands by the following method.

$$EPh_2Cl + [Co(H_2dmg)_2pyX] \xrightarrow{-XCl} [Co(EPh_2)(H_2dmg)_2py]$$

(E=Sb,Bi, X=Cl,Br)

Synthesis of $-PCl_2$ [102] and $-AsMe_2$ [87] complexes has been achieved by the elimination of trimethylsilylchloride.

$$[M(CO)_3cp(SiMe_3)] + PCl_3 \xrightarrow{-SiMe_3Cl} [M(CO)_3cp(PCl_2)]$$

(M=Cr,Mo,W)

Elimination of HCl has resulted in the formation of a -PPhH complex [83].

$$[W(CCMe_3)Cl_3(PEt_3)_2] + PPhH_2 \xrightarrow{-HCl} [W(CCMe_3)Cl_2(PEt_3)_2(PPhH)]$$

1.7(a)(iii) Elimination of Alkali Metal Halides

Extensive use has been made of the elimination of alkali metal halide salts in reactions between group 5B halides and anionic transition metal complexes. Nesmeyanov et al used this method to synthesize a rhenium complex [84].

$$BiPh_2Cl + Na[Re(CO)_5] \longrightarrow [Re(BiPh_2)(CO)_5] + NaCl$$

Cullen et al have also used the method [78]:

$$BiCl_3 + 3Na[Co(CO)_3(PPh_3)] \longrightarrow [Bi\{Co(CO)_3(PPh_3)\}_3] + 3NaCl$$

and the elimination of mercury(II)chloride.

$$2AsCl_3 + [Hg\{Fe(CO)_2(NO)(PPh_3)\}_2] \longrightarrow [Fe(AsCl_2)(CO)_2(NO)(PPh_3)] + HgCl_2$$

Complexes of $-AsMe_2$ have also been prepared [85,86].

$$K[Mn(CO)_4(PR_3)] + AsMe_2Cl \longrightarrow [Mn(AsMe_2)(CO)_4(PR_3)] + KCl$$

Salts of the type $K/Na[M(C_5R_5)(CO)_n]$ (M=Cr,Mo,W,n=3, M=Fe,Ru,n=2, R=H,Me) have been extensively used, particularly by Malisch et al, and the reactions are covered in Figure 1.

The first workers to make use of $LiPR_2$ to produce these complexes were Isslieb and Kratz [133].

$$3KPPh_2.2Z + [M(CO)_3(NH_3)_3] \xrightarrow{-3NH_3} K_3[M(CO)_3(PPh_2)_3] + 6Z$$

(Z=dioxane, M=Cr,Mo,W). It was then realised that the reaction of $LiPR_2$ with transition metal halide complexes was an important synthetic route to three-co-ordinated phosphorus complexes. The reactions using this method are summarised in Figure 2.

Figure 1 Reactions of Group 5B Halides with K/Na[M(CO)$_n$C$_5$R$_5$] salts (M=Cr,Mo,W,n=3; M=Fe,Ru,n=2)

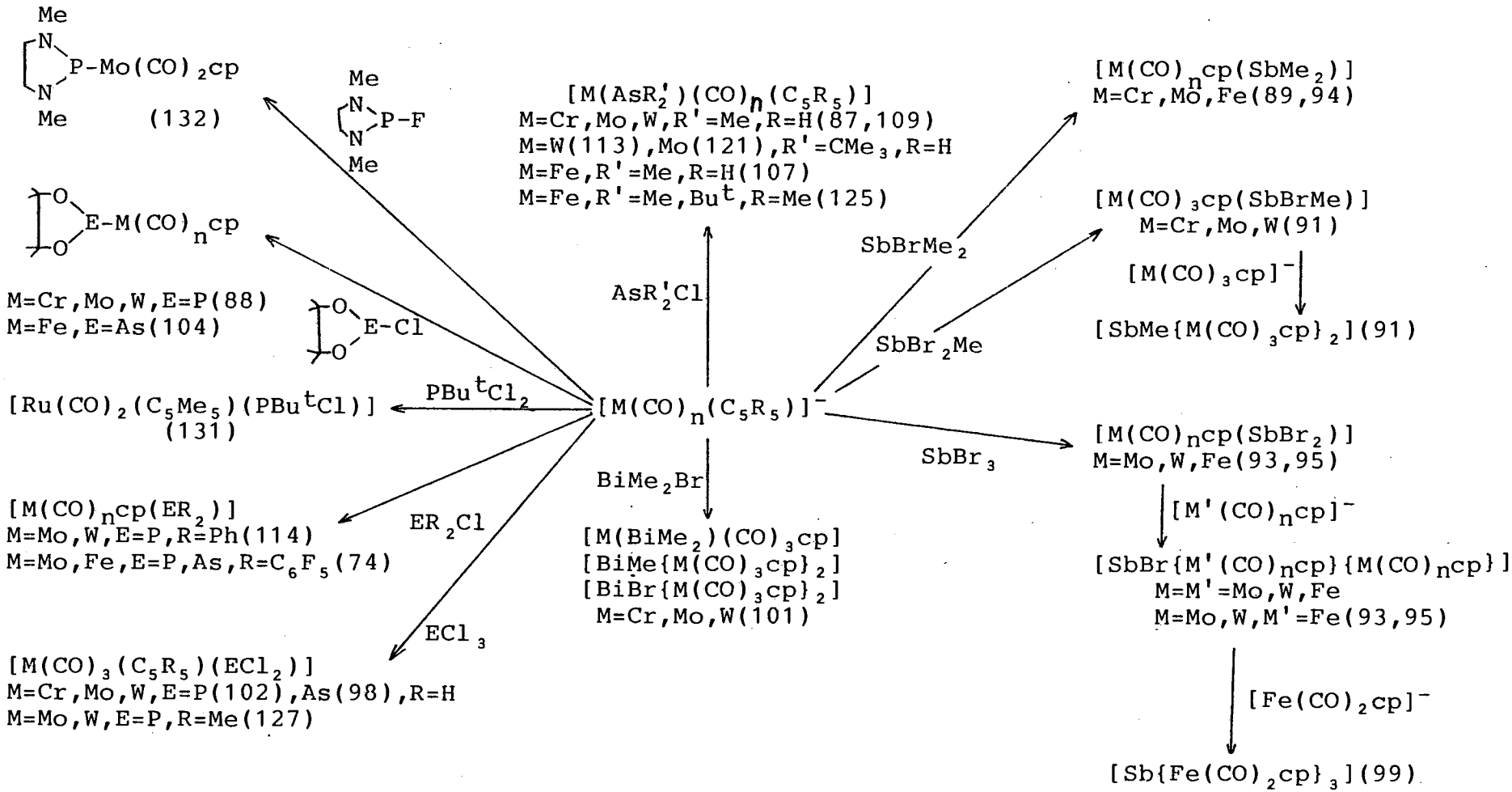
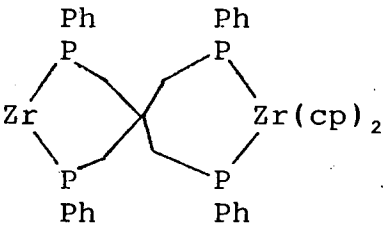


Figure 2 Reactions of MPR_2 with Transition Metal Halide Complexes

$C[CH_2P(M)Ph]_4 + 2[Zr(cp)_2Cl_2] \xrightarrow{-2MCl}$  M=K,Na (134)

$NaPR_2 + [M(cp)_2Cl_2] \xrightarrow{-NaCl} [M(cp)_2(PR_2)_2]$ R=Me,Ph, M=Ti,Zr (135)

$2NaMPh_2 + [Ti(cp)_2Cl_2] \xrightarrow{-2NaCl} [Ti(cp)_2(MPh_2)]$ or $[Ticp(MPh_2)_2]^-$ M=P,As (136)

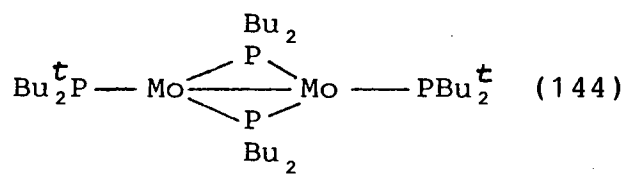
$LiPPh_2 + [Fe(CO)_2cpCl] \xrightarrow{-LiCl} [Fe(CO)_2cp(PPh_2)]$ (137,138)

$MPR'_2 + [TiBr(NR_3)_3] \xrightarrow{-MBr} [Ti(NR_3)_3(PR'_2)]$ M=Li,Na, $R=CH_3$, $R'=C_2H_5$, $Si(CH_3)_3$; $R=R'=C_2H_5$ (139)

$2KPPh_2(2Z) + [Ta(dmpe)_2Cl_2] \xrightarrow{-2KCl} [Ta(dmpe)_2H(PPh_2)_2]$ Z=dioxane (140)

$2LiPR_2 + [M(cp)_2Cl_2] \xrightarrow{-2LiCl} [M(cp)_2(PR_2)_2]$ M=Zr,Hf; R=Et,cy,Ph (141,142)

$LiPcy_2 + [M(thf)_yCl_n] + dme \longrightarrow [Li(dme)][M(Pcy_2)_x]$ see reference for details (143)

$4Li(Bu^t{}_2P) + [Mo_2(OAc)_4] \xrightarrow{-4Li(OAc)}$  (144)

1.7(a)(iv) Deprotonation

Another route to these complexes is the deprotonation of phosphine ligands, using n-butyllithium or methyllithium to produce a lithium salt and butane or methane. The following complexes have all been produced in this manner: $Li[M(CO)_5\{P(C_6F_5)_2\}]$ [145] (M=Cr,Mo), $Li[M(CO)_5(PPh_2)]$ [146] (M=Cr,Mo,W), $Li[Fe(CO)_4(PRPh)]$ [146] (R=Me,Et), $Li[Mn(CO)cp(PPhH)]$ [147], $Li[Cr(CO)_5(PPhH)]$ [147], $Li[Mn(CO)_2(C_5H_4Me)(PPhH)]$ [147], $Li_2[Mo(CO)_4(PMe_2)_2]$ [148], $Li_n[M(CO)_m(PRH)_n]$ [149,150] (M=Mo,R=Ph,m=5,n=1, M=Mo,R=Ph,H,m=4,n=2, M=Fe,R=Ph,m=4,n=2). A neutral species has been made in a similar way, but using a cationic starting complex [151]:

$$[M(CO)_ncp(PPh_2H)][PF_6] \xrightarrow[-C_4H_{10}]{+Bu^nLi} [M(CO)_ncp(PPh_2)] + Li[PF_6]$$

(M=Fe,n=2, M=Mo,n=3).

Deprotonation using the base dbu has also been successful [152]:

$$[Os(CO)_2Cl(PPh_3)_2(PPhH_2)] \xrightarrow{dbu} [Os(CO)_2Cl(PPh_3)_2(PPhH)]$$

The reaction of hydrogen ion with a molybdenum complex also produces a three-co-ordinated phosphorus [153]:

$$[Mo\{P(OCH_3)_3\}_6] \xrightarrow[-CH_3OH]{+H^+} [Mo\{P(OCH_3)_3\}_5\{P(OCH_3)_2\}]^+$$

1.7(a)(v) Oxidative Addition

Oxidative addition to iridium(I), rhodium(I) and platinum(II) centres have been used to prepare three-co-ordinated phosphorus species:

$PF_2X + [Ir(CO)Y(PEt_3)_2] \longrightarrow [Ir(CO)XY(PEt_3)_2(PF_2)]$ (52-54)

(X=H,Y=Br,I; X=Cl,Y=Cl,Br; X=Br,I,Y=Cl,Br,I)

$PF_2X + [Rh(CO)X(PEt_3)_2] \longrightarrow [Rh(CO)X_2(PEt_3)_2(PF_2)]$ (53)

(X=Br,I)

$PCl_3 + [Ir(CO)Cl(PEt_3)_2] \longrightarrow [Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$

(53,55,56)

$PCl_3 + [Rh(CO)Cl(PEt_3)_2] \longrightarrow [Rh(CO)Cl_2(PEt_3)_2(PCl_2)]$ (53)

The reaction of PH_3 with iridium(I) complexes has also given rise to three-co-ordinated phosphorus:

$PH_3 + [Ir(CO)(dmpe)_2]Cl \longrightarrow [Ir(CO)H(dmpe)_2(PH_2)]Cl$ (154)

$PH_3 + [Ir(CO)Cl(PEt_3)_2] \longrightarrow [Ir(CO)ClH(PEt_3)_2(PH_2)]$ (155)

The reactions of PCl_3 and PBr_3 with platinum(II) species are as follows [156]:

$$PCl_3 + [PtClH(PEt_3)_2] \xrightarrow{-HCl} [PtCl(PEt_3)_2(PCl_2)]$$

$$PBr_3 + [PtBrH(PEt_3)_2] \downarrow$$

$$[PtBr_2H(PEt_3)_2(PBr_2)] \downarrow -HBr$$

$$[PtBr(PEt_3)_2(PBr_2)].$$

1.7(b) Reactivity

Most work on the reactivity of three-co-ordinated phosphorus, arsenic, antimony and bismuth has been attempts to form "bridges". Other reactivity such as quaternisation, protonation and reactions with group 6B elements have been examined as well as reactions with dichlorine and dibromine.

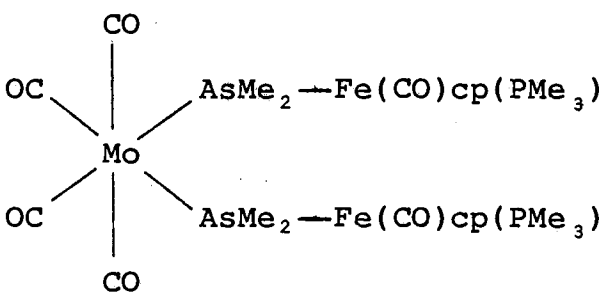
1.7(b)(i) Formation of Bridged Compounds

Successful reactions have been carried out with the following compounds; $BH_3(thf)$ [123,127], $[Mn(CO)_3cp]$ [92,95], $[Fe_2(CO)_9]$ [92,128], $[Ni(CO)_4]$ [97,128], $[W(C_7H_8)(CO)_3]$ [89,94], $[M'(nbd)(CO)_4]$ [89,94,122] (M'=Mo,W), $[M(CO)_6]$ [92], $[M(thf)(CO)_5]$ [89,94,95,98,99,101,103,104,105] (M=Cr,Mo,W), $[M(cod)Cl_2]$ [53,54] (M=Pt,Pd), B_2H_6 [53,54,55,56,155], $[\{M(\eta^6\text{-arene})Cl_2\}_2]$ [53,54,155] (M=Ru,Os, arene=benzene or para-cymene) and sodium napthalenide in thf [142], for example:

$$[Mo(C_5Me_5)(CO)_3(PCl_2)] + BH_3(thf) \xrightarrow{-thf} [Mo(C_5Me_5)(CO)_3\{P(BH_3)Cl_2\}] \quad (127)$$

$$[SbMe\{Cr(CO)_3cp\}_2] + [Fe_2(CO)_9] \xrightarrow[-Fe(CO)_5]{h\nu} [SbMe\{Cr(CO)_3cp\}_2\{Fe(CO)_4\}] \quad (92)$$

$$2[Fe(AsMe_2)cp(CO)(PMe_3)] + [Mo(nbd)(CO)_4] \xrightarrow{-nbd}$$



(122)

1.7(b)(ii) Quaternisation

Reaction of the complexes with alkyl halides has quaternised the group 5B ligand for example [87,88,89,94,100,108,114,115,125,128,152]:

$$[W(AsMe_2)(CO)_2cp(CNMe)] \xrightarrow{MeI} [W(AsMe_3)(CO)_2cp(CNMe)]I \quad (128)$$

The work of Stelzer et al on anionic complexes can be included in this section and is presented in Figure 3. Protonation of these complexes has led to complexes containing $(-PPh_2H)^+$ [114], $(-PPhH_2)^+$ [152] and $(-PHF_2)^+$ groups [53,55,56].

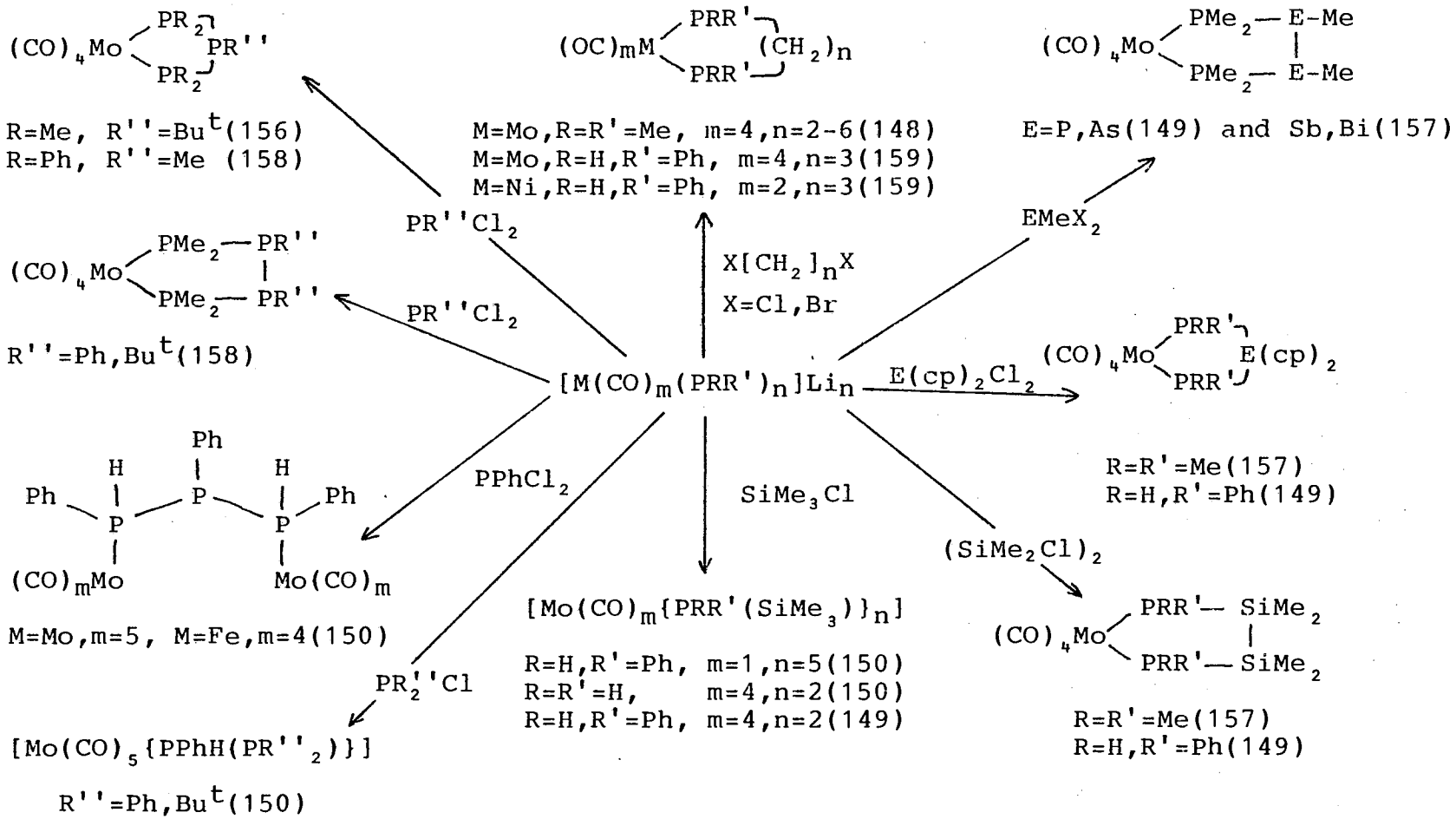
1.7(b)(iii) Group 6B Derivatives

Complexes with ligands containing E=Q bonds (E=P,As,Sb, Q=O,S,Se) have been obtained by reactions of NO [75] and O_2 [53,54] to give P=O bonds and by S_8 and Se_8 to give E=S and E=Se compounds [75,102,105,125,130,52-56]. Reactions of $-PF_2$ groups with H_2E (E=O,S,Se) have produced -PFHE groups [53,54]. With $-PCl_2$ groups, H_2E reaction leads to -PClHSe, -PHSe(SeH), $-PH_2Se$, -PClHS and -PHO(OH) groups [53,55,56].

1.7(b)(iv) Halogens

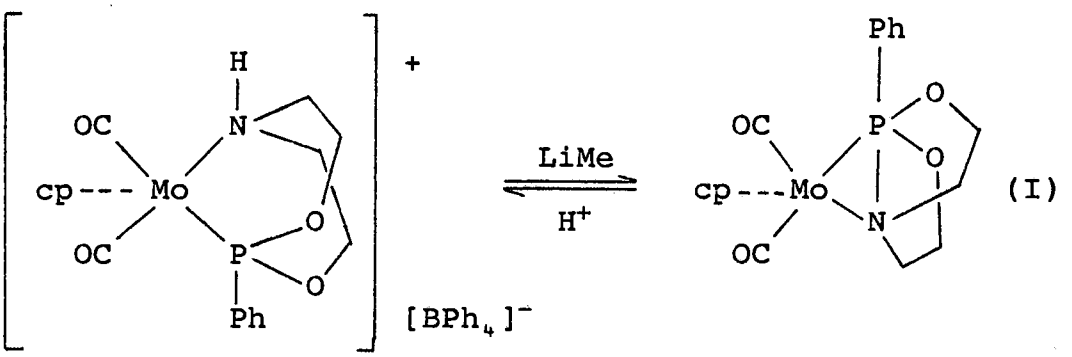
Reactions of three-co-ordinated phosphorus ligands with Cl_2 or Br_2 were often proposed as routes to five-co-ordinated ligands but the species produced were unstable or difficult to characterise [90,91,93,95,109,160]. More recent work by Malisch et al has obtained five-co-ordinated antimony by the reaction of PPh_2Cl with a three-co-ordinated species (see Section 1.8) [117].

Figure 3 Reactions of PR_2 complexes reported by Stelzer et al

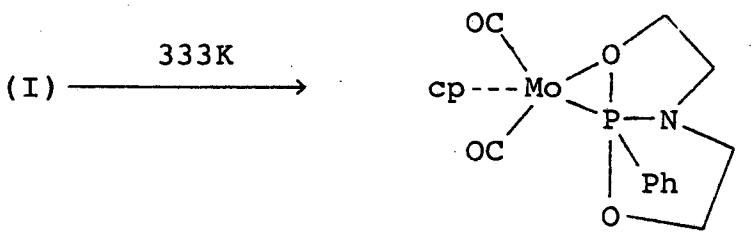


1.8 Transition Metal Complexes of Five-co-ordinated Phosphorus and Antimony

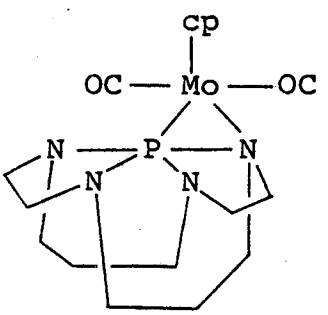
A number of different synthetic routes to these compounds has been attempted, as well as a limited study of the reactivity of the five-co-ordinated products. Aminophosphorane molybdenum adducts have been prepared by Riess et al [161,162].



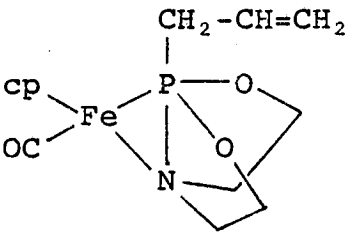
On heating, the compound (I) converts to an isomer.



A cyclamphosphorane molybdenum adduct has been prepared [163]:

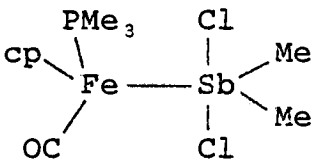


and also the following complex [164]:

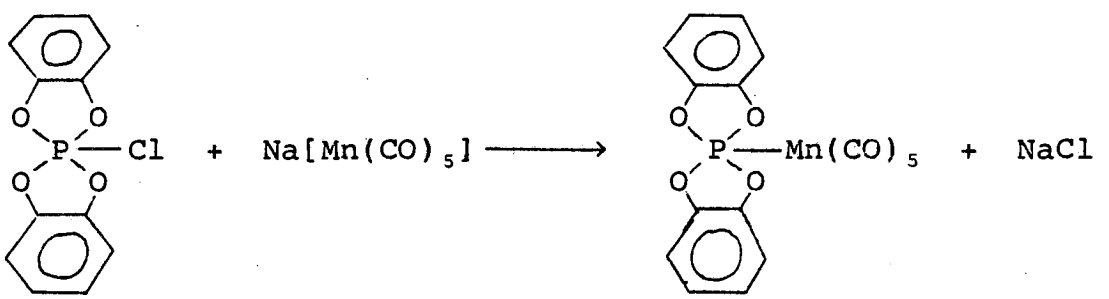


A five-co-ordinated antimony compound has been prepared by Malisch et al [117]:

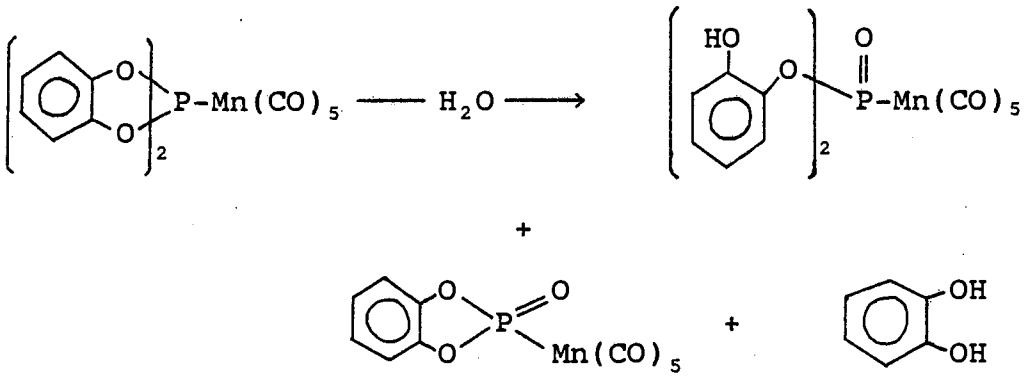
$$[Fe(CO)cp(PMe_3)(SbMe_2)] + PPh_2Cl \xrightarrow{-\frac{1}{2}(PPh_2)_2}$$



The work of Lattman et al has led to another five-co-ordinated phosphorus species [165]:



The same workers have shown that this species can be hydrolysed [166]:



Chapter 2

Reactions of some Main Group Halides with $[Ir(CO)Cl(PEt_3)_2]$

In Chapter 1 we noted that Vaska's compound and its phosphine analogues had undergone a vast range of oxidative and donor addition reactions. The work detailed here was an attempt to widen the range, using multinuclear n.m.r. spectroscopy as the main analytical method.

2.1 Group 3 Halides

2.1(a) Borontrichloride

This reaction was examined as it took place in an n.m.r. tube, and ^{31}P and ^{11}B n.m.r. spectra were recorded at temperatures from 180K to 300K. At 180K the $^{31}P-\{^{1}H\}$ spectrum showed two singlets, at -0.4 p.p.m. (which was from $[Ir(CO)Cl_2H(PEt_3)_2]$ [53]) and at -8.5 p.p.m.. On warming, the singlet at -8.5 p.p.m. broadened steadily (Figure 4) as the temperature increased to 300K. Upon cooling, the peak became sharp again, and this behaviour was found to be reproducible. In a separate experiment, the solvent was removed at 300K and the remaining gum was heated to 330K whilst under vacuum. The species mentioned above was still present on re-examining the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. The ^{11}B n.m.r. spectrum at 300K showed a broad singlet ($W_{\frac{1}{2}} \simeq 550Hz$) at 56.2 p.p.m. which is close to the value for BCl_3 of 47 p.p.m. [167]. At 220K, this peak had broadened ($W_{\frac{1}{2}} \simeq 1600Hz$) and another, but sharp peak ($W_{\frac{1}{2}} \simeq 2Hz$) had appeared at 7.5 p.p.m., which is close to the value [167] for $[BCl_4]^-$. From the evidence of other workers [37,38], it seems likely that BCl_3 would form a donor adduct complex of iridium(I), which may lose BCl_3 in vacuo. The ^{31}P n.m.r. spectra can be

interpreted in different ways.

There may be a simple chemical exchange involving two species, one of which may be present in only a small quantity so we have not seen its ^{31}P resonance. Alternatively if there are two exchanging species in equilibrium, the equilibrium constant may be temperature dependant and one species may predominate at 220K. This would give a sharp resonance at this temperature. As the temperature is increased both species are present and the ^{31}P resonance broadens as exchange occurs. On warming above 300K we might expect the broad resonance to split and sharpen as the rate of chemical exchange increases.

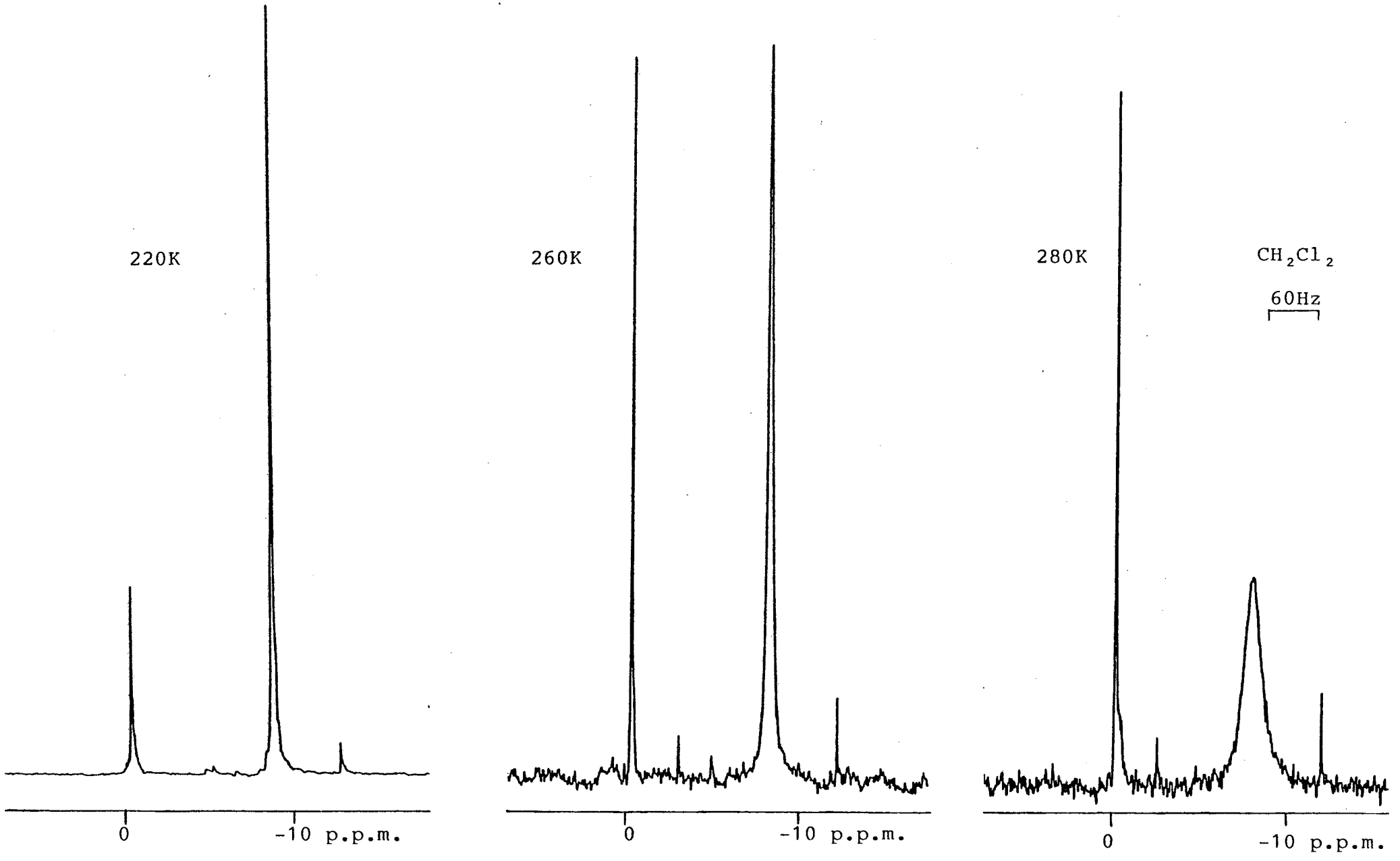
If we propose a species containing boron in the co-ordination sphere of iridium, we can consider another alternative for the line broadening. The boron nucleus may have a short relaxation time at low temperature so that it is effectively decoupled from phosphorus. The ^{31}P resonance would consequently be sharp at low temperature. As the temperature is increased the ^{11}B relaxation time decreases (see Appendix 2) so the phosphorus couples to the boron, giving a broad resonance at 300K. This might split into a 1:1:1:1 quartet as the temperature is increased.

The linewidths at half height for boron donor adduct complexes are typically 100Hz (see Chapter 4), so neither of these resonances are from such a complex. The presence of a small amount of $[BCl_4]^-$ may be explained by the removal of chloride from iridium or the solvent. A

hydrogenchloride impurity in the BCl_3 was discovered to be the reason for some $[Ir(CO)Cl_2H(PEt_3)_2]$.

Isolation of the complex was not possible because of the formation of an intractable gum upon removal of the solvent. In an attempt to observe a corresponding borontrifluoride species, borontrifluoride-diethyletherate was added to $[Ir(CO)Cl(PEt_3)_2]$, but no reaction was observed.

Figure 4 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl(PEt_3)_2]$ + BCl_3



2.2 Group 4 Halides

2.2(a) Silicontetrachloride

No reaction was observed over a period of one month at room temperature according to the $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

2.2(b) Hexachlorodisilane, Si_2Cl_6

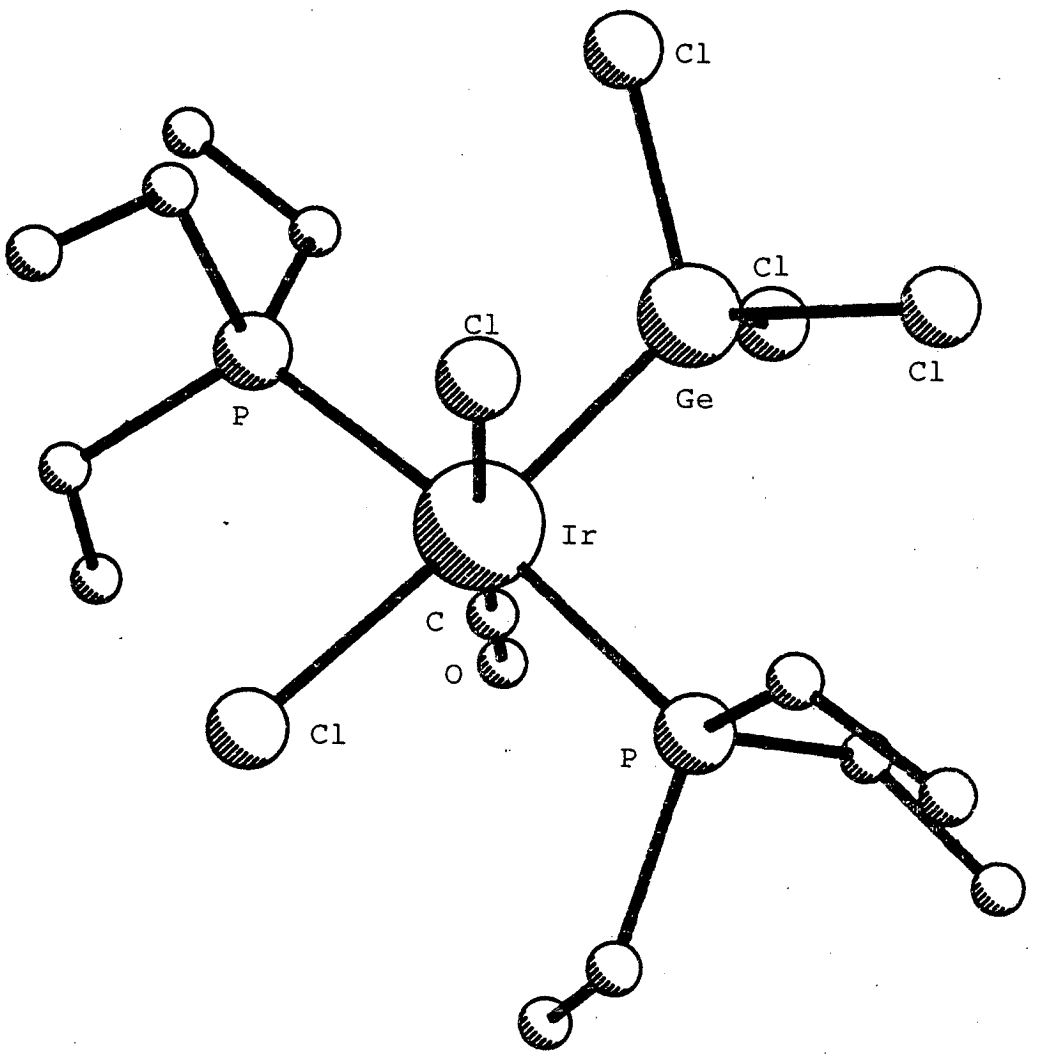
No reaction was observed after two days at room temperature. The sample was then irradiated at 254 mμ for 120 hours in an attempt to cause a reaction by breaking the Si-Si bond. No reaction was observed on examination of a $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

2.2(c) Germaniumtetrachloride

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the solution at 300K showed a singlet at -10.4 p.p.m.. Isolation of the product was successful and it was characterised as $[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$ by elemental analysis, by infra-red spectroscopy and by an X-ray crystal stucture determination [168] (Figure 5). Elemental analysis for carbon and hydrogen was satisfactory for the formulation and the infra-red data were also consistent with the structure; absorptions were observed (among other frequencies) at 2040cm^{-1} (carbonyl stretch [21,46,48]), 364, 377, and 397cm^{-1} (Ge-Cl stretches [169]) and 419cm^{-1} (Ir-P stretch [170]). This is clearly an oxidative addition reaction, but we cannot say whether the addition was *cis* or *trans* since there are two chlorides bound to iridium. The structure is discussed in Appendix 1.

Figure 5

X-ray Crystal Structure of $[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$



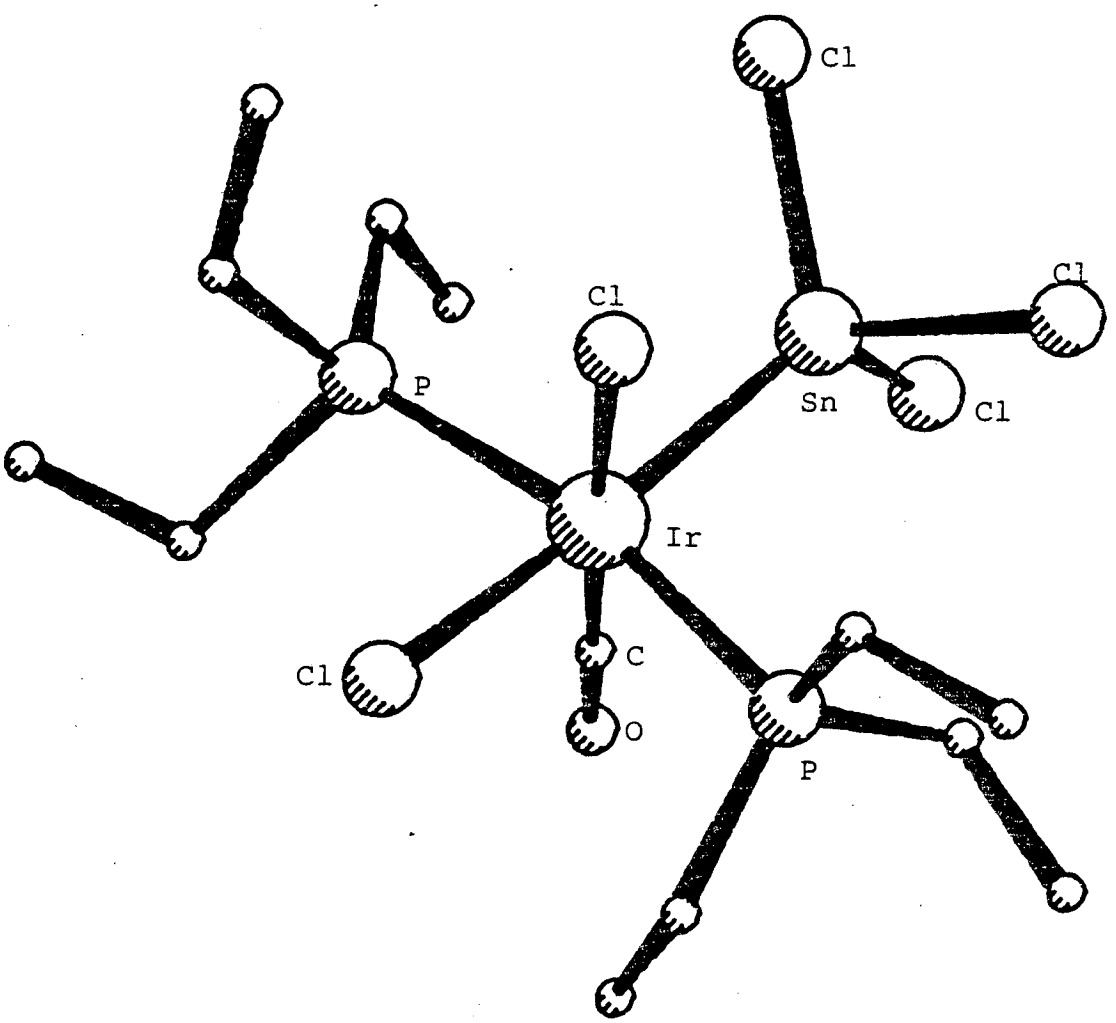
2.2(d) Tintetrachloride

This reaction was initially observed using low temperature $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy. At 180K a singlet with two sets of satellites was observed at -7.7 p.p.m.. On warming to 300K this pattern had moved to -9.9 p.p.m., but was qualitatively unchanged. The satellites were from the isotopes ^{117}Sn and ^{119}Sn, both of which have $I=\frac{1}{2}$ and are about 8% abundant. Molecules without either of these isotopes had singlet ^{31}P resonances and those with these isotopes had doublet resonances. The more intense satellites were from molecules containing ^{119}Sn; $^{2}J(^{119}Sn,^{31}P)$ = 143.8Hz, the others being from ^{117}Sn; $^{2}J(^{117}Sn,^{31}P)$ = 137.5Hz. On observing the ^{119}Sn n.m.r. spectrum a triplet resonance at -460.1 p.p.m., $^{2}J(^{119}Sn,^{31}P)$ = 146.1Hz was found. Elemental analysis of the solid isolated from the reaction mixture was consistent with a 1:1 mixture of $[Ir(CO)Cl(PEt_3)_2]$ and $SnCl_4$. The results of an X-ray crystal structure determination are given in Figure 6 [171] and the structure is discussed in Appendix 1. Infra-red data were similar to those obtained from the reaction of $[Ir(CO)Cl(PEt_3)_2]$ with $GeCl_4$, showing absorptions at 2040cm^{-1} (CO stretch), 327, 335, 340, and 352 cm^{-1} (Sn-Cl stretches [48,172]).

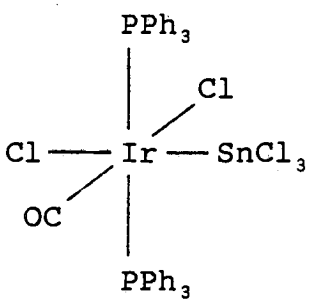
The results of the reaction with Vaska's compound show that two carbonyl stretching frequencies are obtained in the infra-red spectrum at 2080 and 2040cm^{-1} [48,49]. Pregosin et al [49] have examined the ^{31}P and ^{119}Sn n.m.r. spectra and found one species present at room

Figure 6

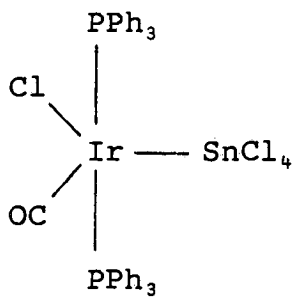
X-ray Crystal Structure of $[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$



temperature, but two at 160K. They are however unable to contribute to the structural chemistry other than to say that the phosphines are equivalent in both compounds and that the n.m.r. evidence is consistent with the structures (I) and (II)



(I)



(II)

2.3 Group 5 Compounds

2.3(a) Phosphorustrichloride

This reaction had been previously investigated, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showing a doublet and a triplet pattern from the species $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ (Figure 7) [53]. The ^{13}C chemical shift of the carbonyl group has now been found to be 163 p.p.m. (Table 3) and an X-ray crystal structure determination of this compound confirms the structure as trans-$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ (Figure 8) [168] and the details of the structure are discussed in Appendix 1.

2.3(b) Phosphoruspentachloride

Equimolar quantities of $[Ir(CO)Cl(PEt_3)_2]$ and PCl_5 in dichloromethane solution were examined by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy at 180K and the spectra showed that reaction had begun. Small quantities of $[Ir(CO)Cl_2H(PEt_3)_2]$, $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and

Figure 7 24.2MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl$_2$(PEt$_3$)$_2$(PCl$_2$)]

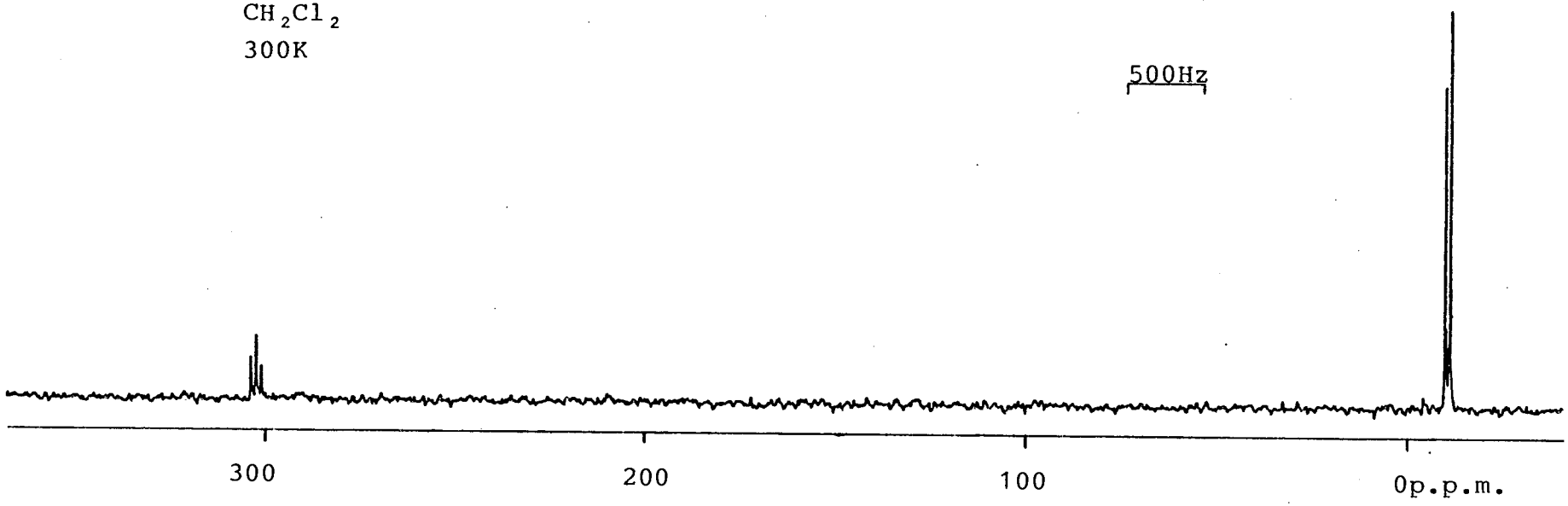


Figure 8

X-ray Crystal Structure of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$

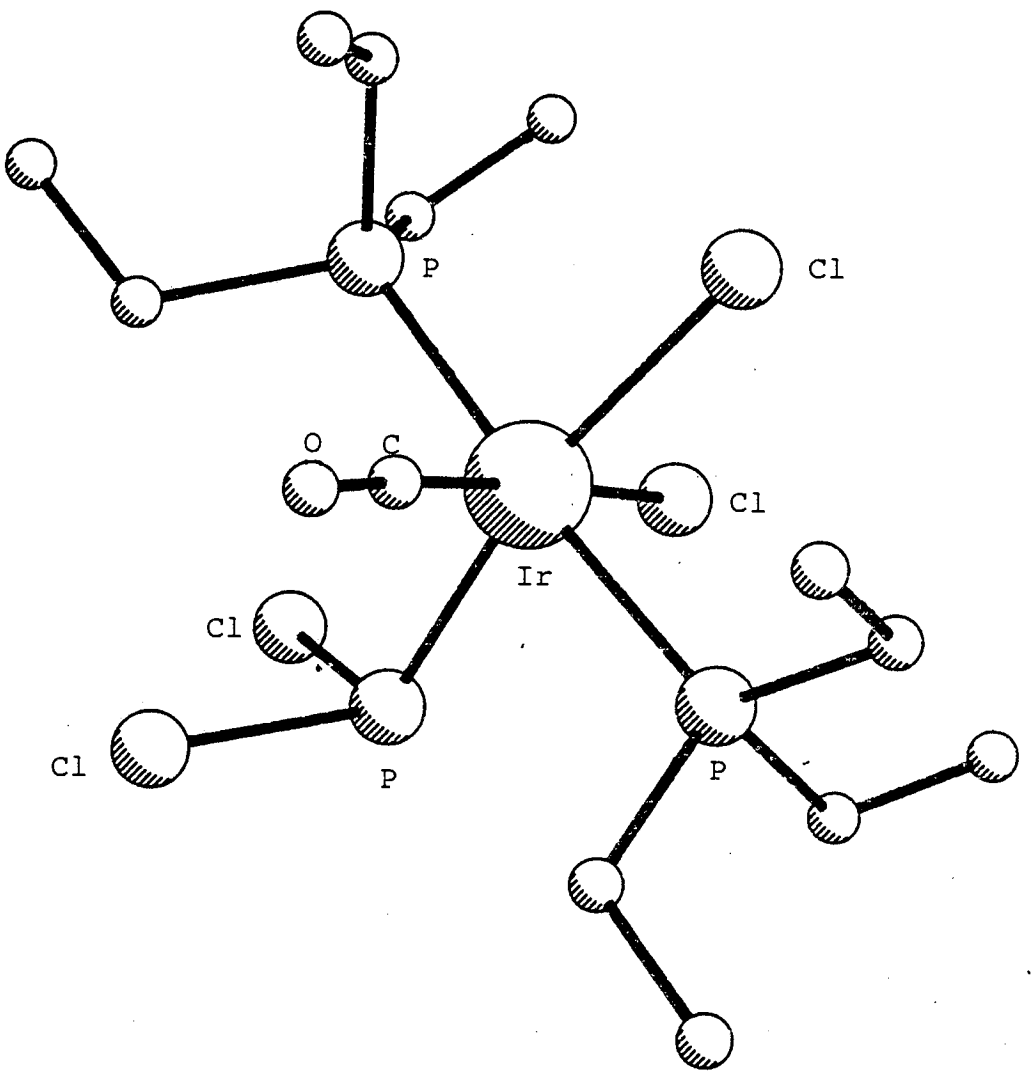
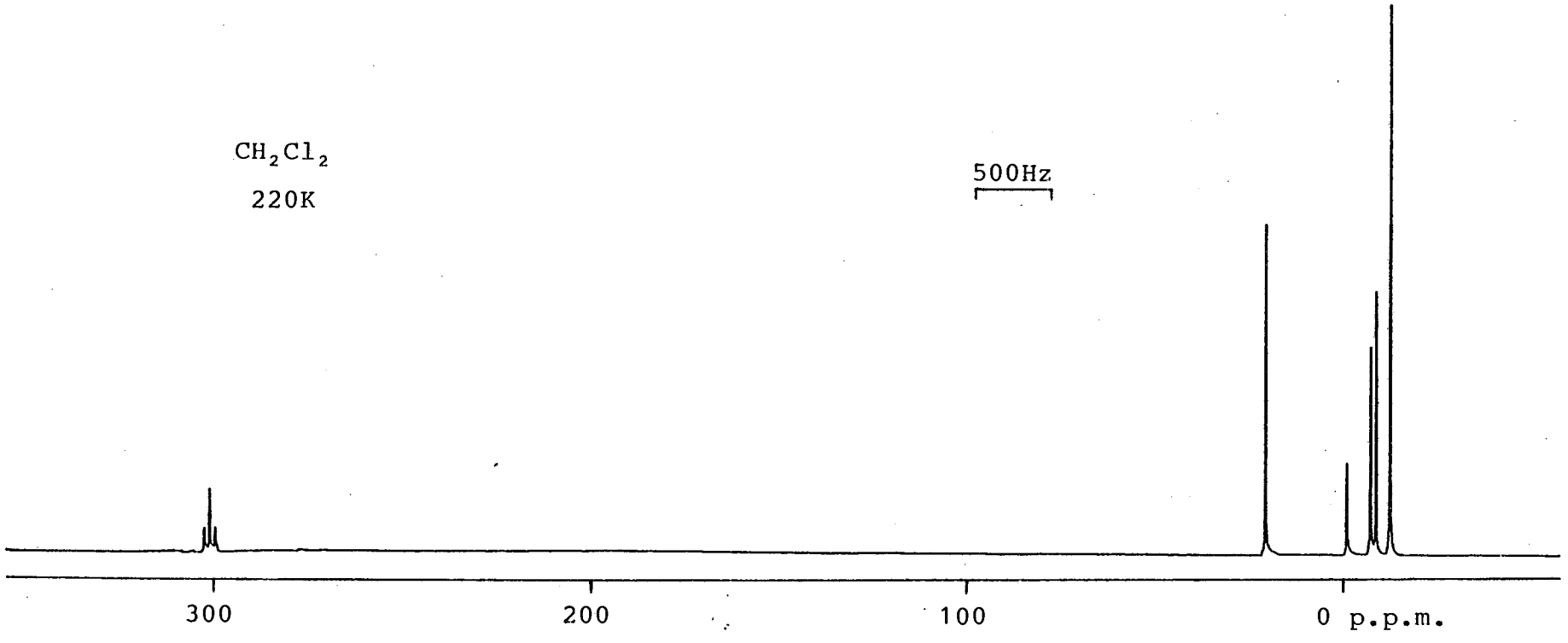


Figure 9 24.2MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl(PEt_3)$_2$] + PCl_5



trans-$[Ir(CO)Cl_3(PEt_3)_2]$ were present but much $[Ir(CO)Cl(PEt_3)_2]$ remained. As the reaction mixture was warmed to 220K, the resonances from $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and trans-$[Ir(CO)Cl_3(PEt_3)_2]$ increased in intensity while that from $[Ir(CO)Cl(PEt_3)_2]$ decreased. The $^{31}P-\{^1H\}$ n.m.r. spectrum is shown in Figure 9 and the results are consistent with the following reaction:

$$2[Ir(CO)Cl(PEt_3)_2] + PCl_5 \longrightarrow [Ir(CO)Cl_2(PEt_3)_2(PCl_2)] + \text{trans-}[Ir(CO)Cl_3(PEt_3)_2]$$

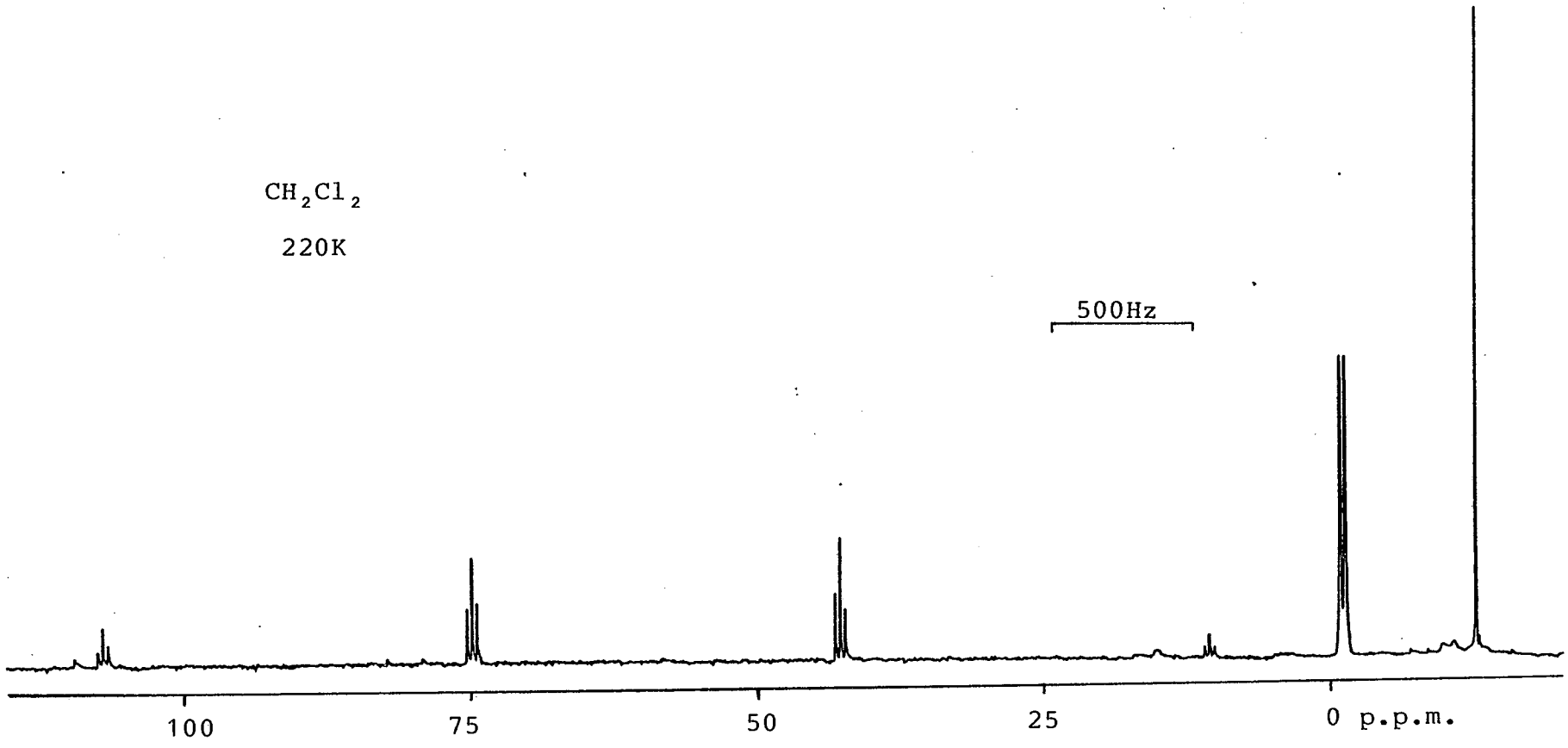
2.3(c) Phosphorylchloride, $POCl_3$

Initially there was no reaction according to the $^{31}P-\{^1H\}$ n.m.r. spectrum, but after the solution had remained at 300K for one month, reaction had occurred to give trans-$[Ir(CO)Cl_3(PEt_3)_2]$ and $[Ir(CO)Cl_2(PEt_3)_2-(PCl_2)]$. The $^{31}P-\{^1H\}$ n.m.r. spectrum also showed a singlet at 111.9 p.p.m., which may be assigned [173] as P_4O_6.

2.3(d) Dichlorotrifluorophosphorane, PCl_2F_3

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 190K showed a singlet from trans-$[Ir(CO)Cl_3(PEt_3)_2]$ along with a wide quartet ($^1J(P',F)$ = 1302Hz) of triplets ($^2J(P,P')$ = 17.9Hz) at 58.3 p.p.m. and a broad doublet at -0.9 p.p.m. (Figure 10). The ^{19}F n.m.r. spectra showed a wide doublet of triplets ($^3J(P,F)$ = 2.5Hz) at -25.0 p.p.m.. This latter species is clearly a "$P_2,P'F_3$" system. The reaction was repeated, but after allowing reaction to occur at 190K, an equimolar quantity of

Figure 10 40.5MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl(PEt_3)_2]$ + PCl_2F_3



borontrichloride was added. There was no change in the $^{31}P-\{^{1}H\}$ spectrum at 180K, and the ^{11}B n.m.r. spectrum showed a sharp peak at 7.4 p.p.m. ($W_{\frac{1}{2}} \simeq 2Hz$) which may be assigned [167] as $[BCl_4]^-$. Whilst we cannot say what other ligands are bound to iridium, the structure $[Ir(CO)Cl_2(PEt_3)_2(P'F_3)][BCl_4]$ (vii) is consistent with the results. Further evidence for this compound is discussed in the consideration of the reaction of dichlorine with $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ (see Section 3.1(b)(ii)).

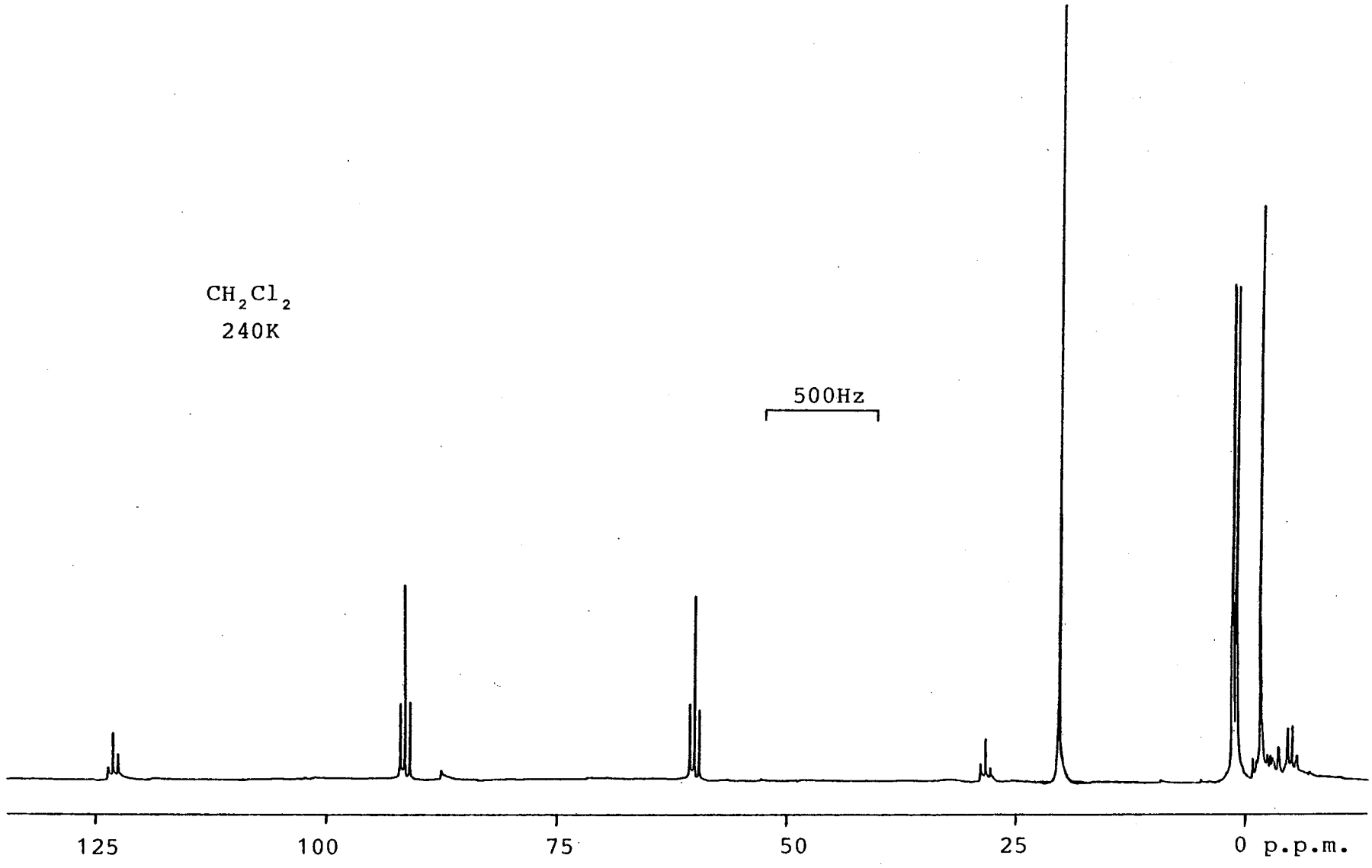
2.3(e) Chlorotetrafluorophosphorane, $PClF_4$

At 190K the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed the species $[Ir(CO)Cl(PEt_3)_2]$, $[Ir(CO)Cl_2(PEt_3)_2(P'F_3)]^+$ (vii) and a septet at -144 p.p.m. assigned [174] to $[PF_6]^-$. No resonances from a "$P_2,P'F_4$" species were observed in this reaction. If such a species was produced, its reaction with free fluorophosphine may have caused formation of the cation.

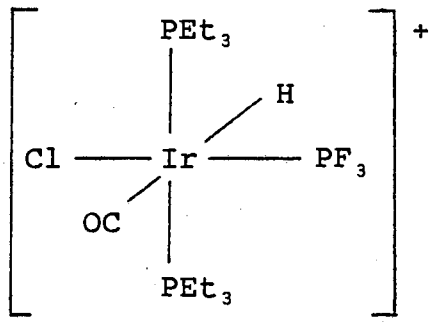
2.3(f) Tetrafluorophosphorane, PF_4H

This reaction was initially investigated by ^{31}P n.m.r. spectroscopy and at 190K the proton decoupled spectrum showed four species (Figure 11); two were easily identified as unreacted $[Ir(CO)Cl(PEt_3)_2]$ and $[Ir(CO)Cl_2H(PEt_3)_2]$. The third gave a quintet of doublets at -140.4 p.p.m. [$^{1}J(P,F_a)$ = 822Hz, $^{1}J(P,F_b)$ = 732Hz], with a further doublet splitting ($^{1}J(P,H)$ = 592Hz) when proton coupling was retained. The ^{19}F and ^{1}H n.m.r. spectra confirmed the identity of this [175] as $[PF_5H]^-$.

Figure 11 40.5MHz-^{31}P-{^{1}H}-spectrum (part) of [Ir(CO)Cl(PEt_3)$_2$] + PF_4H



The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the fourth species consisted of a quartet ($^{1}J(P',F)$ = 1267Hz) of triplets ($^{2}J(P,P')$ = 21.0Hz) at 75 p.p.m. and a broad doublet at 1 p.p.m.. When proton coupling was retained, the quartet of triplets showed a further doublet splitting. The ^{1}H n.m.r. spectrum of this species showed a doublet of triplets of quartets at -9.8 p.p.m., characteristic of a hydride <u>trans</u> to a carbonyl group. The ^{19}F n.m.r. spectrum showed a wide doublet of triplets of doublets, so the complex contained a $-PF_3$ group coupled to two equivalent $-PEt_3$ groups and to a hydride. The compound decomposed above 240K. The structure below is consistent with these results.



$\delta P'$ =	74.4 p.p.m.	$^{1}J(P',F)$ =	1267 Hz
δP =	1.14p.p.m.	$^{2}J(P,P')$ =	21.0Hz
δF =	-14.8 p.p.m.	$^{2}J(P,H)$ =	12.2Hz
δH =	-9.8 p.p.m.	$^{2}J(P',H)$ =	21.0Hz
		$^{3}J(F,H)$ =	9.0Hz
		$^{3}J(P,F)$ =	3.5Hz

The n.m.r. parameters were obtained in dichloromethane at 240K.

It is not possible to say whether oxidative addition of PF_4H occurred, since no "$H,P_2,P'F_4$" species

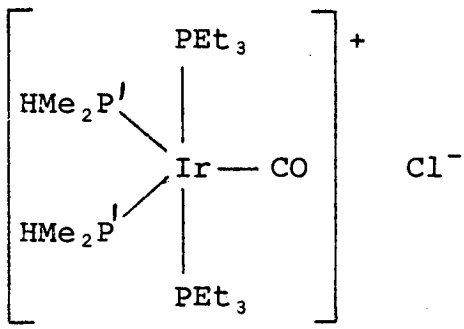
was observed. If such a species were formed, its reaction with a molecule of free PF_4H may give both the products observed in this experiment.

2.3(g) Dimethylphosphorylchloride, PMe_2ClO

No reaction was observed between $[Ir(CO)Cl(PEt_3)_2]$ and PMe_2ClO.

2.3(h) Dimethylphosphine

The $^{31}P-\{^1H\}$ n.m.r. spectrum of an equimolar mixture of $[Ir(CO)Cl(PEt_3)_2]$ and PMe_2H showed some unreacted $[Ir(CO)Cl(PEt_3)_2]$ and a species whose spectrum consisted of two triplets, -14.0 and -94.0 p.p.m. [$^2J(P,P') = 23.0Hz$]. Further work [155] on similar reactions suggests that the stucture of the species may be



2.3(i) Dimethylphosphinouschloride, PMe_2Cl

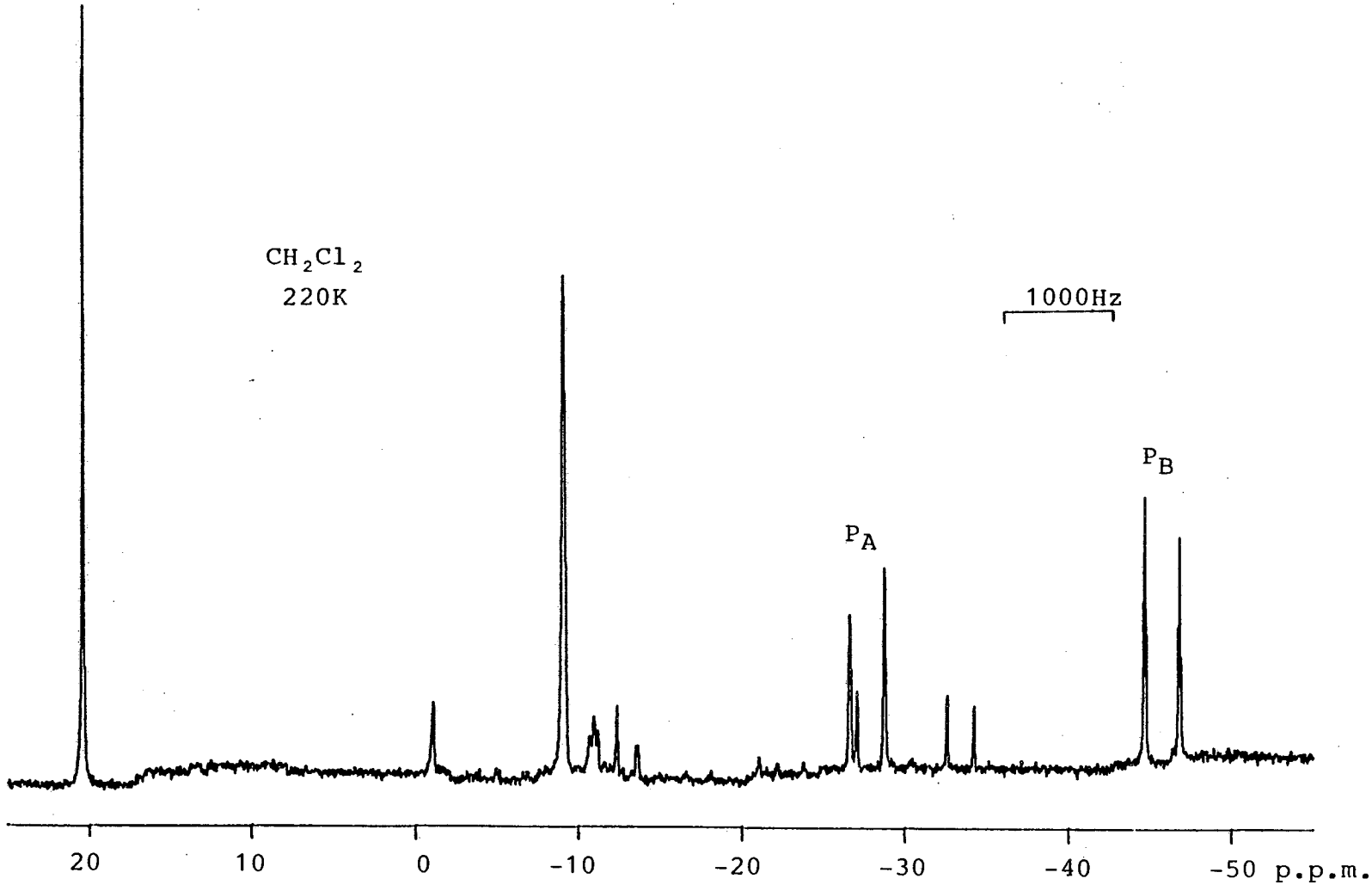
Observation of the $^{31}P-\{^1H\}$ n.m.r. spectrum at 180K of an equimolar mixture of $[Ir(CO)Cl(PEt_3)_2]$ and PMe_2Cl gave the following results; much $[Ir(CO)Cl(PEt_3)_2]$ was present, although some reaction had occurred to give two species in low yield, one of which was $[Ir(CO)Cl_2H(PEt_3)_2]$; the spectrum of the other appeared to consist of two triplets at 55 and -18 p.p.m.. When another spectrum was obtained a few minutes later at the same temperature, these triplets had decreased in

intensity and had disappeared on warming to 190K. Other resonances then appeared and at 220K three major species were present (see Figure 12): $[Ir(CO)Cl(PEt_3)_2]$ (a singlet at about 20 p.p.m.), $[Ir(CO)Cl_2H(PEt_3)_2]$ (a singlet at about -1 p.p.m.) and a third whose spectrum consisted of a doublet of doublets at about -9 p.p.m. with an associated AB pattern of triplets to lower frequency [176]. Full n.m.r. parameters are given later.

Triethylphosphine resonances are usually found between +5 p.p.m. and -20 p.p.m., so the resonance at -9 p.p.m. in the spectrum of the new species may be assigned to two equivalent triethylphosphine groups. The AB pattern is not from the $-PEt_3$ groups. The size of the AB coupling indicates that P_A and P_B are mutually trans. Whilst warming to 300K, the triplet coupling collapsed at 273K, only to reappear on cooling below 263K. This may be because of a dissociation process, possibly a P-Cl bond on a bound $-PMe_2Cl$ group, or the breaking of one of the bonds to iridium. Addition of chloride did not alter the temperature at which the collapse of coupling occurred, but with added chloride the compound decomposed when the solution was warmed to 300K.

The ^1H n.m.r. spectrum of this mixture at 220K was also obtained. There is a simple triplet in the hydride region at -16.8 p.p.m., $^2J(P,H)$ = 11.4Hz, which is from $[Ir(CO)Cl_2H(PEt_3)_2]$. At higher frequency there was a doublet at about 2.2 p.p.m. and a doublet of doublets at about 1.5 p.p.m. (Figure 13). Full parameters are given

Figure 12 145.8MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl(PEt$_3$)$_2$] + PMe$_2$Cl



later.

Selective decoupling whilst observing the ^{1}H n.m.r. spectrum gave the following results; the protons at 1.5 p.p.m. showed a large coupling to P_B and a small coupling to P_A (Figure 13). The protons at 2.2 p.p.m. show coupling to P_B only. It would seem reasonable that these resonances are from PCH_3 protons since the couplings observed are all P,H couplings. We feel it is unlikely that the $^{2}J(P,H)$ couplings are not resolved, so we assign the resonance at 2.2 p.p.m. to P_BMe and those at 1.5 p.p.m. to P_AMe protons. This means that the 1.5 p.p.m. resonance shows a $^{4}J(P,H)$ larger than the $^{2}J(P,H)$ value, as given later.

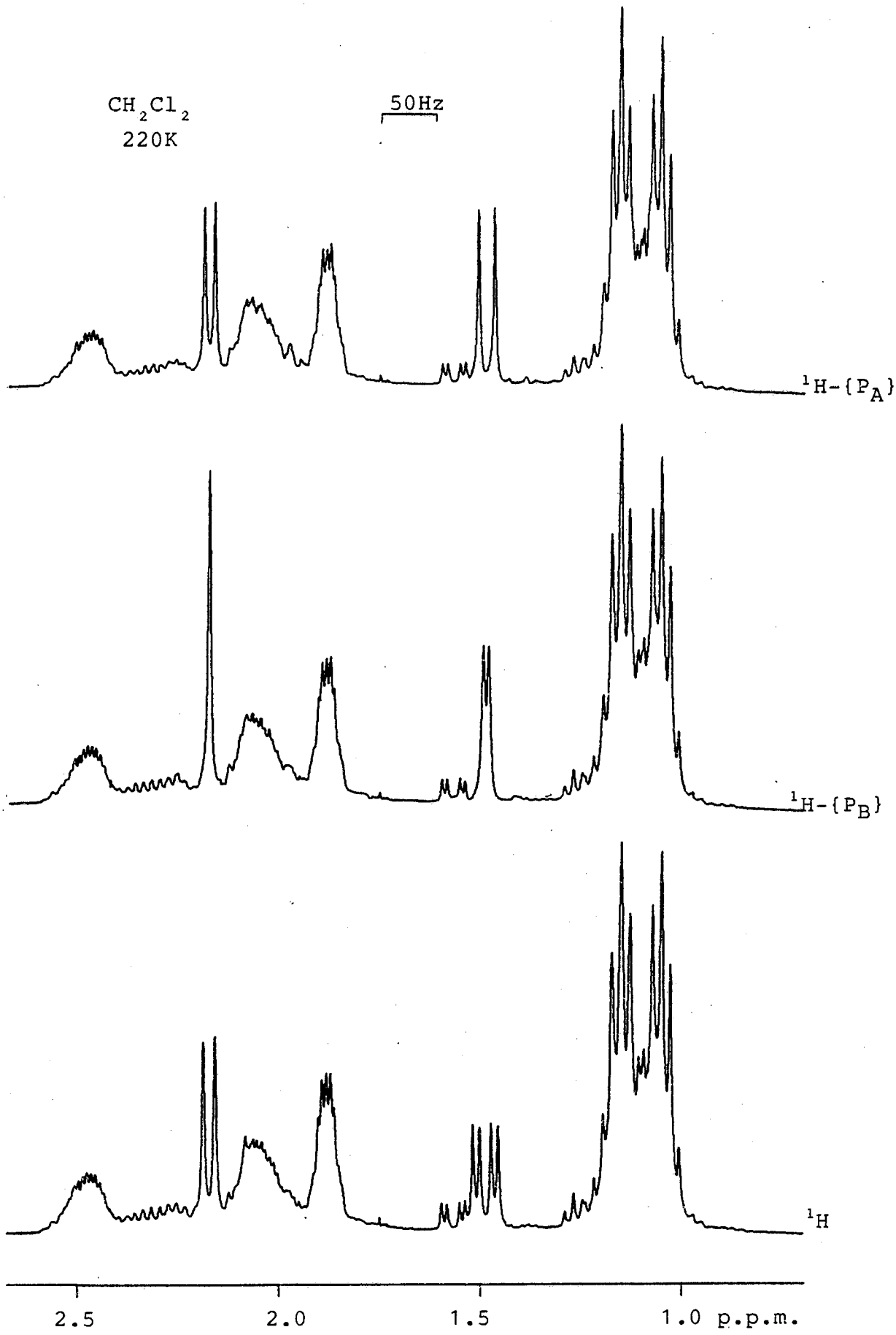
The groups containing P_A and P_B must be different; they may be $-PMe_2Cl$ and $-PMe_2$. There are few examples of $-PMe_2$ ligands [135,148] and the only published phosphorus chemical shift is for <u>cis</u>-$[Mo(CO)_4(PMe_2)_2]Li_2$ which occurs at +94.5 p.p.m. [148]. It is not clear which sign convention for chemical shifts is used in this reference, but we suspect it is opposite to ours, giving a chemical shift of -94.5 p.p.m.. Chemical shift data of which we are more certain are given below [114]:

<u>Compound</u>	<u>δPPh_2/p.p.m.</u>
$[W(CO)_3cp(PPh_2)]$	-63.3
$[Mo(CO)_3cp(PMe_3)(PPh_2)]$	-31.9
$[W(CO)_3cp(PMe_3)(PPh_2)]$	-55.9

These complexes are quite different from those used in this work, but the analogous complexes of $-PCl_2$ show ^{31}P

Figure 13

360MHz-^{1}H-spectrum of [Ir(CO)Cl(PEt$_3$)$_2$] + PMe$_2$Cl



chemical shifts in the same range as $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ [102,127].

Compound	δPCl_2/p.p.m.
$[Cr(CO)_3cp(PCl_2)]$	421
$[Mo(CO)_3cp(PCl_2)]$	394
$[W(CO)_3cp(PCl_2)]$	362
$[Mo(CO)_3(C_5Me_5)(PCl_2)]$	403
$[W(CO)_3(C_5Me_5)(PCl_2)]$	373
$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$	304

A comparison of the ^{31}P chemical shifts of PPh_2X and PMe_2X shows that at least the direction of change of chemical shift on changing X can be predicted [173]:

Compound	X=Cl	X=Br	X=H
PMe_2X	94	90	-99
PPh_2X	80	70	-41

It would seem reasonable therefore to suggest a $-PMe_2$ group as a ligand.

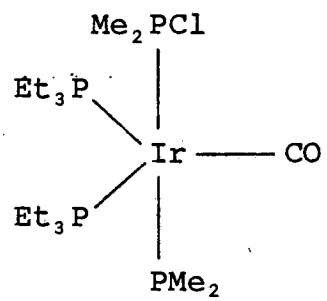
The published ^{31}P n.m.r. data on $-PR_2Cl$ groups bound to a metal is restricted to $-PPh_2Cl$ groups:

Compound	δPPh_2Cl	Reference
free PPh_2Cl	80	173
cis-$[Mo(CO)_4(PPh_2Cl)_2]$	126.4	177
trans-$[Mo(CO)_4(PPh_2Cl)_2]$	137.4	177
$[Ru_2Cl_4(PPh_2Cl)_5]$	145.7,134.5,126.1	178
cis-$[Ru(PPh_2Cl)_2(S_2PMe_2)_2]$	137.0	179
cis-$[Os(PPh_2Cl)_2(S_2PMe_2)_2]$	67.6	180
$[Os(PPh_2Cl)_2(S_2PPh_2)_2]$	66.4	180

Proton n.m.r. data on $[Mo(CO)_5(PMe_2Cl)]$ is as follows:

δH = 2.02 p.p.m., $^2J(P,H)$ = 3.8Hz [181]. The phosphorus shifts above cover a wide range and do not preclude the assignment of a peak at -28 p.p.m. to a bound $-PMe_2Cl$ group in the complex we are discussing.

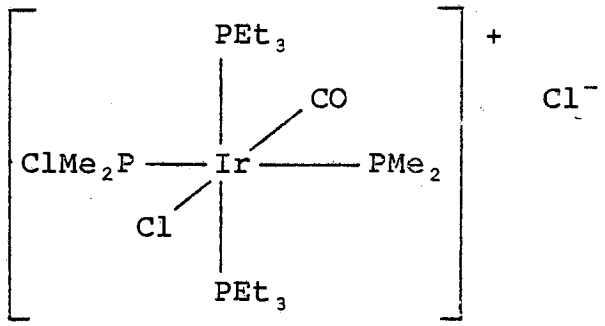
Assuming that the AB pattern is caused by the groups $-P_AMe_2Cl$ and $-P_BMe_2$, we can consider some stuctures for the product. In order to determine the nature of the other ligands we tested for release of carbonmonoxide from the solution but found none, so we propose that a carbonyl group is present. The species is also known to be a "P_2,P_A,P_B" spin system with P_A and P_B mutually <u>trans</u>. One possible product is the iridium (I) species:



This species is doubtful since its formation requires the elimination of dichlorine. This cannot have happened since there is no $[Ir(CO)Cl_3(PEt_3)_2]$, and unreacted $[Ir(CO)Cl(PEt_3)_2]$ is still present (see Section 2.5).

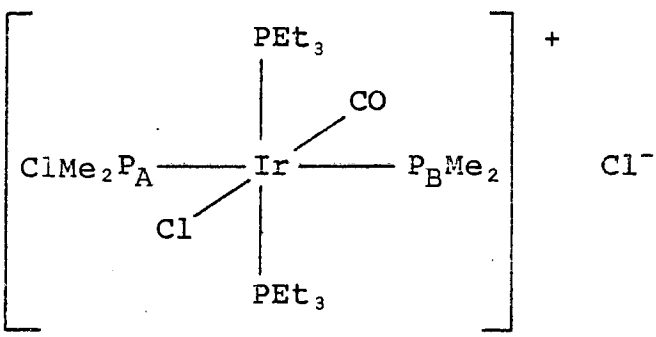
An iridium(II) species is unlikely since it would be paramagnetic and have a marked effect on the n.m.r. spectra. A five-co-ordinated iridium(III) species is also unlikely since it would probably be trigonally bipyramidal and therefore paramagnetic.

Another possible product is:



which could be obtained by oxidative addition of PMe_2Cl across the P-Cl bond, followed by displacement of chloride by another PMe_2Cl molecule. Alternatively, two PMe_2Cl molecules may co-ordinate, displacing a chloride to give a five-co-ordinated iridium(I) species which could then undergo intra-molecular oxidation producing the iridium(III) species given above.

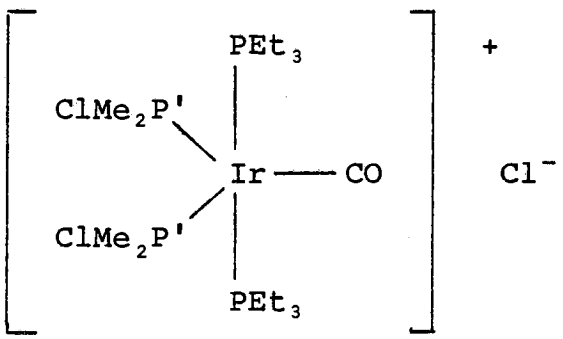
The proposed structure and n.m.r. parameters for a product of the reaction of PMe_2Cl and $[Ir(CO)Cl(PEt_3)_2]$ are as follows:



δP = -9.2 p.p.m.	$^2J(P_A,P_B)$	= 311	Hz
δP_A = -28.0 p.p.m.	$^2J(P,P_A)$	= 8.6	Hz
δP_B = -45.9 p.p.m.	$^2J(P,P_B)$	= 10.9	Hz
$\delta P_A C\underline{H}$ = 1.48 p.p.m.	$^2J(P_A,P_A C\underline{H})$	= 6.1	Hz
	$^4J(P_B,P_A C\underline{H})$	= 16.3	Hz
$\delta P_B C\underline{H}$ = 2.17 p.p.m.	$^2J(P_B,P_B C\underline{H})$	= 10.6	Hz
	$^4J(P_A,P_B C\underline{H})$	not resolved.	

The parameters were recorded in dichloromethane at 220K.

We then examined the reaction of two moles of PMe_2Cl per mole of iridium and the $^{31}P-\{^1H\}$ n.m.r. spectrum at 180K showed that reaction had begun. The two triplet resonances which had been observed before were present and also some $[Ir(CO)Cl(PEt_3)_2]$. The proton spectrum showed (amongst other resonances) a doublet at 1.6 p.p.m. which was assigned to the PC<u>H</u> protons of a bound $-PMe_2Cl$ group. The compound is thought to be that illustrated below:



δP = -17.6 p.p.m.

$\delta P'$ = 55.9 p.p.m. $^2J(P,P')$ = 12.3Hz

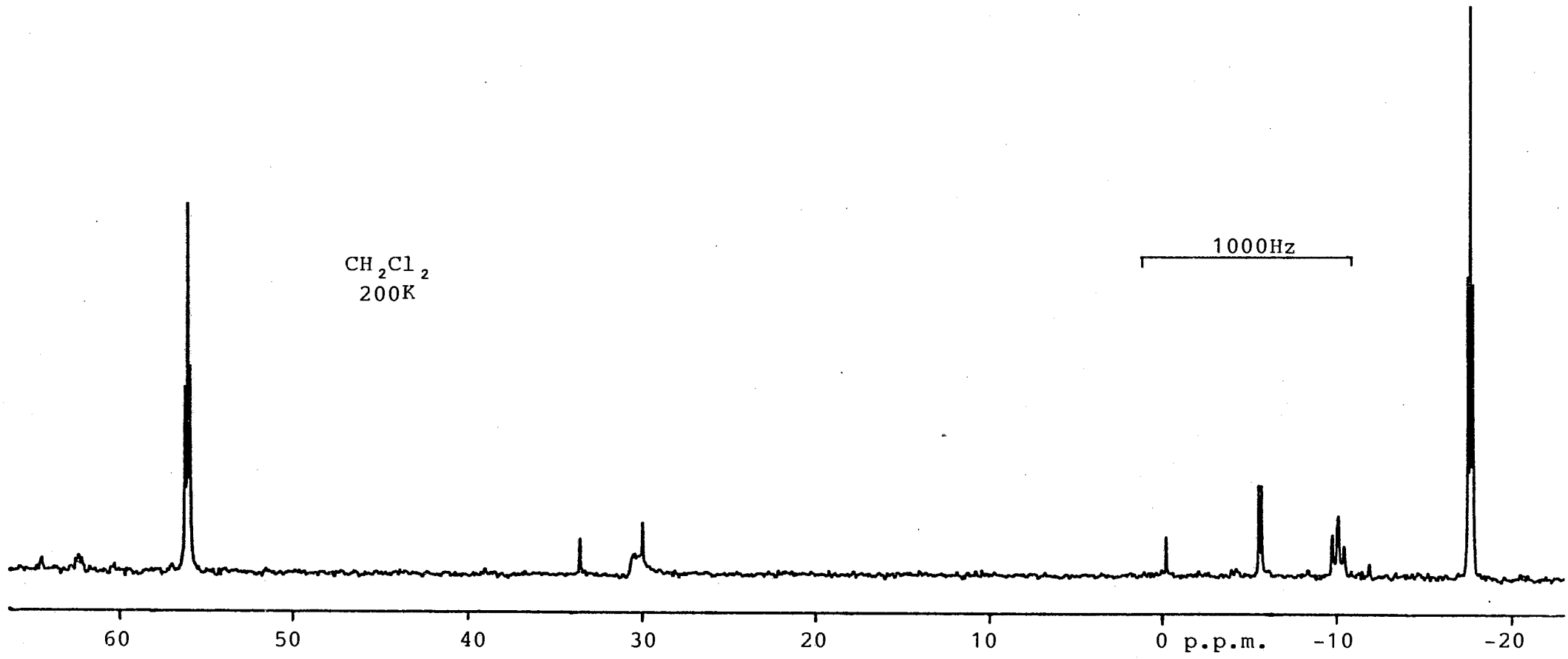
$\delta P'C\underline{H}$= 1.58 p.p.m. $^2J(P,P'C\underline{H})$ = 8.1Hz

The parameters were recorded at 200K in dichloromethane.

The reaction was allowed to continue slowly and by 200K all the $[Ir(CO)Cl(PEt_3)_2]$ had disappeared (Figure 14). At 210K further reaction occurred; the species giving the AB pattern and doublet of doublets (see above) was one of the products, together with a number of other species, but we shall not discuss these further. Intra-molecular oxidation of iridium in the five-co-ordinated complex may have occurred to produce the six-co-ordinated complex.

We also added BCl_3 to the 2:1 reaction mixture

Figure 14 81.0MHz-$^{31}P-\{^{1}H\}$-spectrum of $[Ir(CO)Cl(PEt_3)_2]$ + $2PMe_2Cl$



after it had been warmed to 250K to allow reaction to occur. The ^{31}P n.m.r. spectrum at 180K did not appear to have changed and the ^{11}B n.m.r. spectrum at this temperature showed a sharp resonance at -6.9 p.p.m. ($W_{\frac{1}{2}} \simeq 3.4Hz$) which is clearly not from $[BCl_4]^-$. The identity of the species giving rise to this resonance is not known.

2.3(j) Arsenictrichloride

This reaction was also investigated using ^{31}P n.m.r. spectroscopy, and the proton decoupled spectrum of the solution at 300K showed a singlet at -8.9 p.p.m.. Isolation of a solid from the solution was successful and infra-red absorptions occurred (amongst other frequencies) at 2038cm^{-1} (assigned as CO stretch) and at 355 and 328cm^{-1}, which may be assigned to As-Cl stetches [182]. The formulation $[Ir(AsCl_2)(CO)Cl_2(PEt_3)_2]$ is consistent with partial elemental analysis.

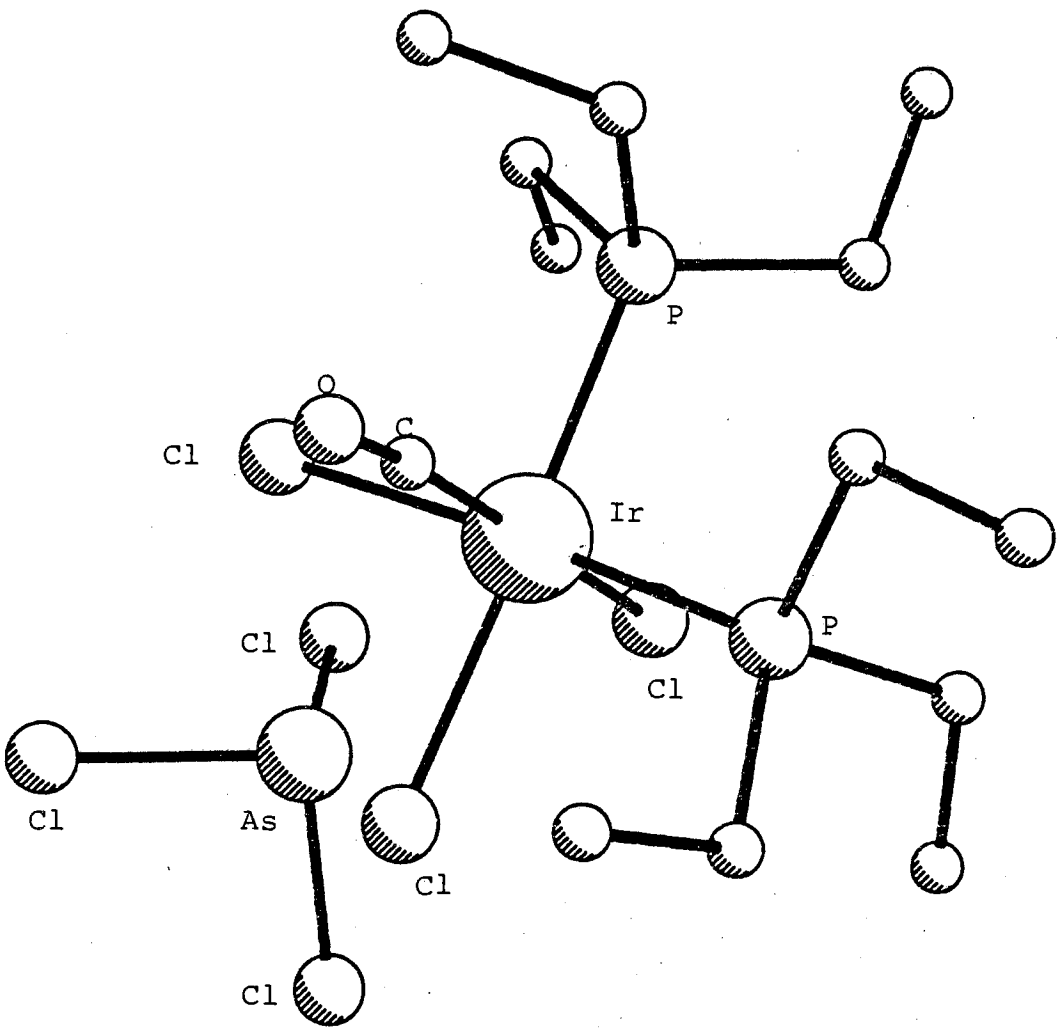
Repeated attempts to grow crystals have led to the production of three different species. The first crystals obtained gave diffraction patterns which indicated that the structure was isomorphous with that of $[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$ [171] (see Section 2.2(c)). Unfortunately the crystals decomposed before a set of intensity data could be collected. More crystals from the same sample were also investigated a number of weeks later using X-ray diffraction and a structure was obtained [168] (Figure 15). The material is a lattice adduct of $AsCl_3$ and fac-$[Ir(CO)Cl_3(PEt_3)_2]$. The $AsCl_3$ group is situated

in the centre of the face formed by three chlorine atoms and the structure is discussed further in Appendix 1. The species may have been formed following decomposition of an Ir-As species, or by the association of an $AsCl_3$ molecule with fac-$[Ir(CO)Cl_3(PEt_3)_2]$, the latter being formed by chlorination of $[Ir(CO)Cl(PEt_3)_2]$. All further attempts have led to crystals which have diffraction patterns identical to those of fac-$[Ir(CO)Cl_3(PEt_3)_2]$ [171].

The chemical shift of fac-$[Ir(CO)Cl_3(PEt_3)_2]$ is similar to that obtained in this reaction (see Section 2.5). However, if chlorination of $[Ir(CO)Cl(PEt_3)_2]$ by $AsCl_3$ were to occur, we would expect insoluble arsenic compounds as by-products, but there is no evidence for these. The crystallisation process may also be the cause of decomposition of any Ir-As species, so on the evidence above it would seem possible that $[Ir(AsCl_2)(CO)Cl_2(PEt_3)_2]$ has been formed.

Figure 15

X-ray Crystal Structure of fac-[Ir(CO){$Cl_3(AsCl_3)$}$(PEt_3)_2$]



2.4 Group 6 Chlorides

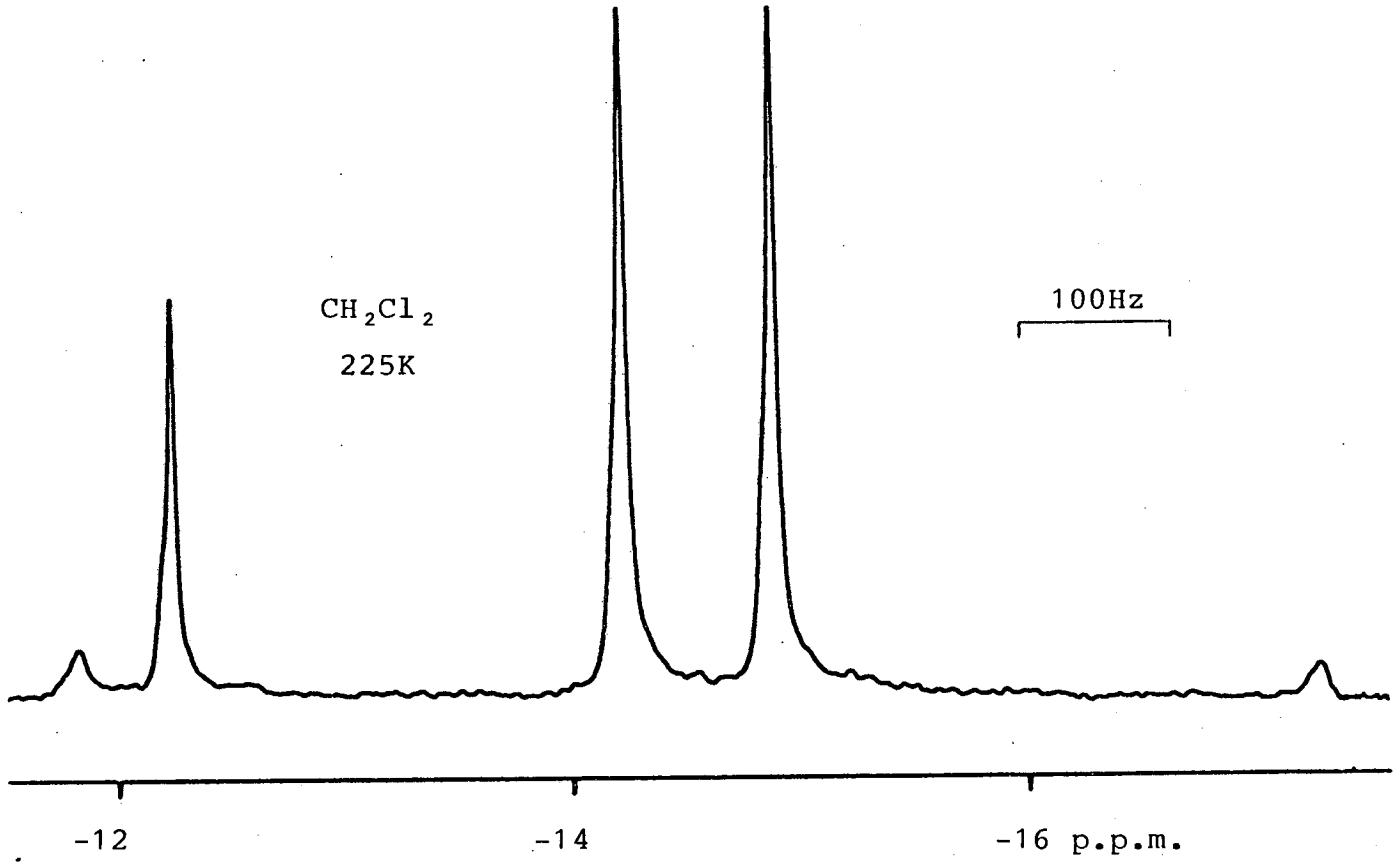
2.4(a) Sulphurdichloride, SCl_2

Examination of the $^{31}P-\{^1H\}$ n.m.r. spectrum of the solution at 300K showed some trans-$[Ir(CO)Cl_3(PEt_3)_2]$ and singlets at -12.7 and -15.3 p.p.m.. The latter resonance is believed to be from the proposed $[Ir(CO)Cl_2(PEt_3)_2(SSCl)]$ (see Section 2.4(b)), so the resonance at -12.7 p.p.m. (which remained a singlet whilst cooling to 180K) is from an unknown species, possibly $[Ir(CO)Cl_2(PEt_3)_2(SCl)]$. A solid was isolated from the reaction mixture and the formulation $[Ir(CO)Cl_2(PEt_3)_2(SCl)]$ is consistent with the results of partial elemental analysis. In attempts to isolate crystals from this reaction mixture, we have only been able to produce fac-$[Ir(CO)Cl_3(PEt_3)_2]$ (see Section 2.5). This brings the analysis figures into doubt, since this compound would have a similar carbon and hydrogen content to $[Ir(CO)Cl_2(PEt_3)_2(SCl)]$. The crystallisation may however prove useful in the purification of the proposed sulphur-containing product of the reaction, which remains in solution.

2.4(b) Disulphurdichloride, S_2Cl_2

At 225K, the $^{31}P-\{^1H\}$ n.m.r. spectrum of the solution showed an AB pattern [176] ; δP_A = -13.6, δP_B = -15.6 p.p.m.; $^2J(P_A,P_B)$ = 360.1Hz (Figure 16). In addition there were singlets from $[Ir(CO)Cl_2H(PEt_3)_2]$ at -0.8 p.p.m. and trans-$[Ir(CO)Cl_3(PEt_3)_2]$ at -12.2 p.p.m.. As the sample was warmed the AB pattern coalesced at 250K,

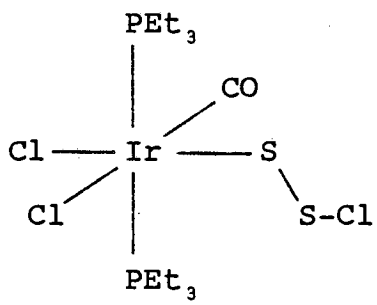
Figure 16 145.8MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl(PEt$_3$)$_2$] + S_2Cl_2



and at 300K the resonance was a sharp singlet at -15.3 p.p.m.. It would seem that this species was also observed in the reaction of $[Ir(CO)Cl(PEt_3)_2]$ with SCl_2, which is consistent with the equilibrium between the sulphur chlorides:

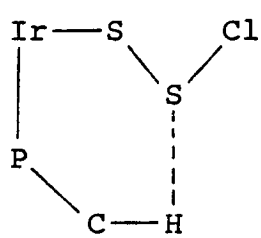
$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2.$$

The inequivalence of the triethylphosphine groups may result from restricted rotation of the -SSCl group about the Ir-S bond or the -SCl group about the S-S bond. The phosphines would be equivalent whenever the two sulphur atoms were in the plane formed by the carbonyl and chlorine ligands.



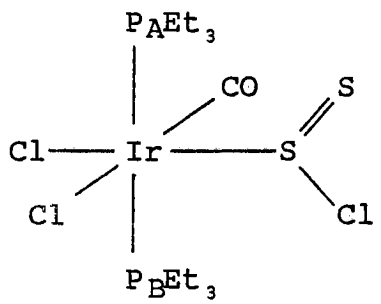
This restricted rotation may arise simply from the bulk of the ligands on iridium although this was not found for similar complexes containing bulky $-PH_2[Ru(p\text{-cymene})Cl_2]$ groups [183].

There may be some interaction between one of the phosphines and the -SSCl group, such as hydrogen bonding.



As the temperature is raised, the -SSCl group would be able to rotate freely, passing the special position frequently enough to render the phosphines equivalent on the n.m.r. time scale.

Alternatively the inequivalence might be caused by the presence of a chiral atom bound to iridium as shown in the following structure:



Inversion of the lone pair would break the chirality, which may be why the AB pattern coalesces, but the barrier to such inversion is usually higher than the coalescence temperature would suggest. Another mechanism to break the chirality may be an equilibrium between straight and ~~balanced~~ branched chain forms of the molecule [184].

At low temperatures the rate of conversion might be slowed and the more stable form, which would have to be the branched chain, would predominate giving rise to a chiral sulphur. In a similar way to the reaction of SCl_2 we were only able to produce crystals of fac-$[Ir(CO)Cl_3(PEt_3)_2]$ from the solutions (see Section 2.5). However this may be useful in purifying the proposed sulphur-containing

product of the reaction, which remains in solution.

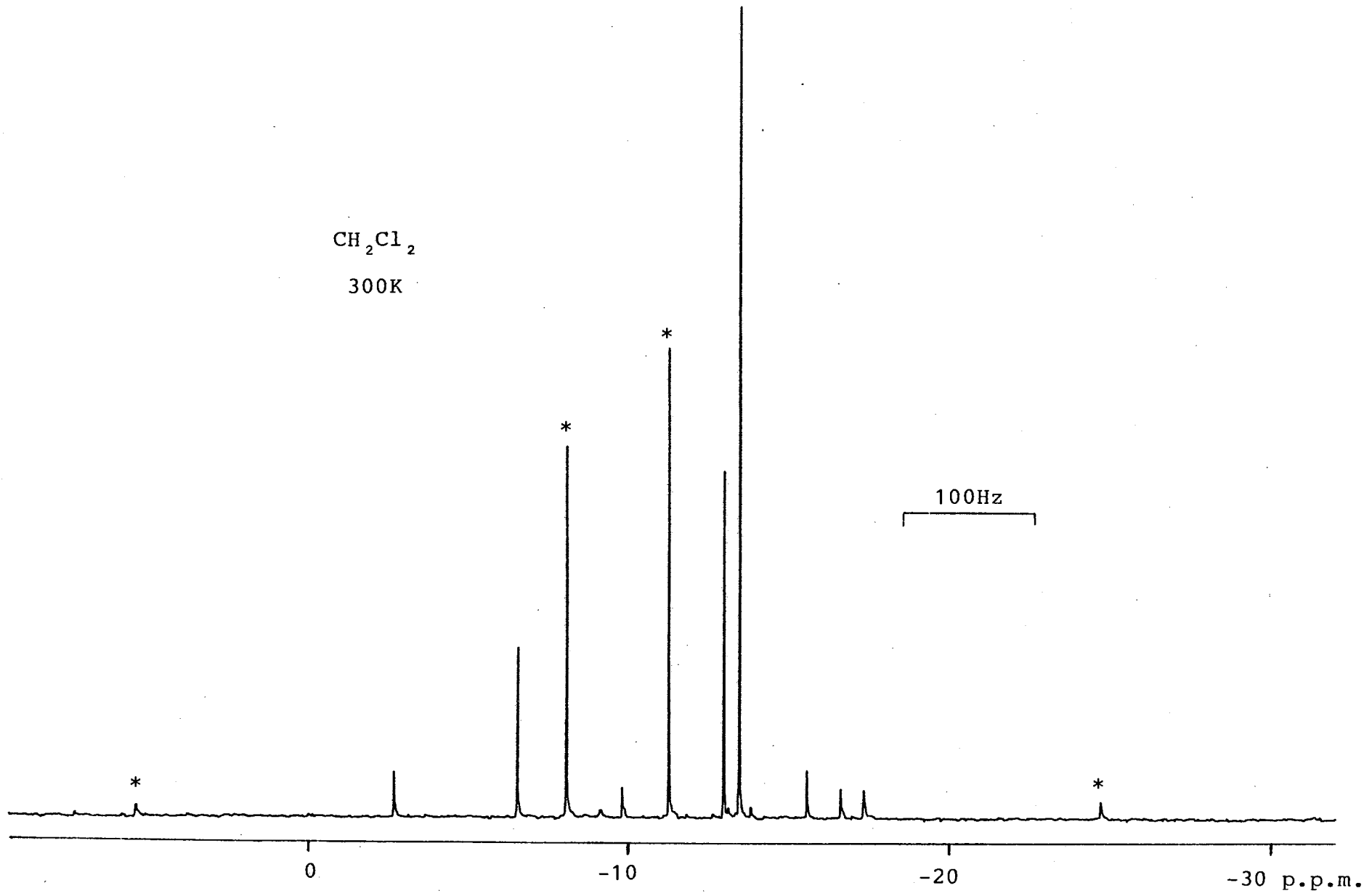
2.4(c) Benzenesulphenylchloride, SPhCl

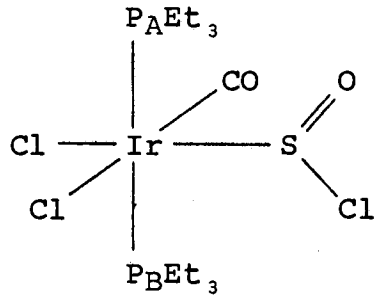
The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the solution showed some $[Ir(CO)Cl_2H(PEt_3)_2]$, and a weak singlet at -8.6 p.p.m.. The major product of this reaction gave an intense singlet at -15.3 p.p.m.. Partial elemental analysis of a solid isolated from the reaction was not consistent with the formulation $[Ir(CO)Cl_2(PEt_3)_2(SPh)]$, but the $^{31}P-\{^{1}H\}$ n.m.r.spectrum obtained on re-dissolving the solid did not correspond with any of the peaks in the original spectrum. The compound may have decomposed before analysis.

2.4(d) Thionylchloride, SCl_2O

According to $^{31}P-\{^{1}H\}$ n.m.r. spectra, reaction had already occurred by 180K, and other than temperature dependent shifts, the spectrum was unaltered between 180 and 380K. Compounds present were $[Ir(CO)Cl_2H(PEt_3)_2]$ (-2.4 p.p.m.), trans-$[Ir(CO)Cl_3(PEt_3)_2]$ (-13.2 p.p.m.), the proposed $[Ir(CO)Cl_2(PEt_3)_2(SCl)]$ (-12.7 p.p.m.) (see Section 2.4(a)), an unassigned singlet (-6.3 p.p.m.) and an AB pattern [176] ; δP_A = -4.6, δP_B = -14.4 p.p.m., $^2J(P_A,P_B)$ = 324.5 Hz (marked with asterisks in Figure 17). Such a pattern could be caused by a chiral sulphur atom co-ordinated to iridium rendering the phosphines inequivalent. The value of the coupling constant is indicative of trans phosphines. The following structure, an oxidative addition product, is consistent with the results.

Figure 17 24.2MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl(PEt_3)$_2$] + SCl_2O





Crystals were isolated from the reaction mixture, but none was suitable for X-ray crystal structure analysis. Examination of these crystals by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy showed that they were fac-$[Ir(CO)Cl_3(PEt_3)_2]$. It may be possible to use this crystallisation to purify and isolate the compound which gives rise to the AB pattern.

2.4(e) Sulphurylchloride, SO_2Cl_2

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 300K consisted of resonances from three species, $[Ir(CO)Cl_2H(PEt_3)_2]$, $[Ir(CO)Cl(PEt_3)_2(SO_2)]$ [53] and trans-$[Ir(CO)Cl_3(PEt_3)_2]$. It would appear that $[Ir(CO)Cl(PEt_3)_2]$ has reduced the S(VI), resulting in both donor and oxidative addition.

2.4(f) Sulphurdioxide

This reaction is well known [19], but the ^{31}P chemical shift is not reported for $[Ir(CO)Cl(PEt_3)_2(SO_2)]$. At 300K the shift was +10.6 p.p.m..

2.4(g) Dioxygen

This product is also well known [185], but there is no published ^{31}P n.m.r. data. The chemical shift of $[Ir(CO)Cl_2(O_2)(PEt_3)_2]$ at 300K was +3.6 p.p.m..

2.4(h) Selenyl chloride, $SeOCl_2$

Room temperature reaction yielded a solution

which was dark green in colour and this gave a $^{31}P-\{^{1}H\}$ n.m.r. spectrum consisting of two singlets of approximately equal intensity at -13.17 and -13.29 p.p.m.. This spectrum was also obtained on a higher field spectrometer which showed that these resonances were not part of an AB pattern. Consequently the singlet at -13.29 p.p.m. was assigned as trans-$[Ir(CO)Cl_3(PEt_3)_2]$. The singlet at -13.17 p.p.m. cannot be from the oxidative addition product of $SeOCl_2$ since this would give an AB pattern. The singlet in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum may have ^{77}Se satellites $^{2}J(Se,P) = 5.9Hz$, but this must be regarded as tentative as we do not have any ^{77}Se n.m.r. spectra of this solution.

2.4(i) Diseleniumdichloride, Se_2Cl_2

The compound $SeCl_2$ is not stable in the liquid phase, but Se_2Cl_2 is, and its reaction with $[Ir(CO)Cl(PEt_3)_2]$ produced large amounts of red precipitate which may be Se_8. No further work has been done on this reaction.

2.4(j) Benzeneselenylchloride, SePhCl

The reaction between SePhCl and $[Ir(CO)Cl(PEt_3)_2]$ was investigated by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy. At 300K the spectrum consisted of a singlet at -17.9 p.p.m. with possible ^{77}Se satellites, $^{2}J(Se,P) = 4.3Hz$. We have no ^{77}Se n.m.r. data. Attempts at isolation of this species led to the formation of intractable oils, so we cannot say what the structure of this species is.

2.5 Dichlorine

The reaction of Vaska's compound with dichlorine [29,68,69] and the synthesis of the three isomers of $[Ir(CO)Cl_3(PEt_3)_2]$ are discussed in the literature [186-188], but not the reaction of dichlorine with $[Ir(CO)Cl(PEt_3)_2]$.

Examination of the $^{31}P-\{^1H\}$ n.m.r. spectrum of the solution at 300K showed a singlet at -13.18 p.p.m. and the methyl region of the ^1H n.m.r. spectrum showed a quintet pattern indicative of trans phosphines [189]. Crystallisation produced two forms of crystals, one of which had an X-ray crystal structure showing fac-$[Ir(CO)Cl_3(PEt_3)_2]$ [168] (Figure 18), the other showing trans-$[Ir(CO)Cl_3(PEt_3)_2]$ [168] (Figure 19).

On re-dissolving crystals of the trans isomer we found a $^{31}P-\{^1H\}$ n.m.r. spectrum identical to that mentioned above. Crystals of the fac isomer re-dissolved to show a singlet at -8.95 p.p.m. at 300K and the ^1H n.m.r. spectrum in the methyl region showed an overlapping doublet of triplets, consistent with cis phosphines [189].

In the investigation of the reaction of triethylphosphine with chloroiridous acid and carbonmonoxide Chatt et al [186] showed that trans-$[Ir(CO)Cl_3(PEt_3)_2]$ was the stable product, but that this isomerised to the fac isomer over a period of three months. Later Shaw et al [188] showed that the isomerisation of trans-$[Ir(CO)Cl_3(PEt_2Ph)_2]$ to the fac form was a photolytic process, taking 96 hours. They

stated that it was likely that the isomerisation of the triethylphosphine complex was also light-induced. In order to test this we observed the effect of natural light on a solution of the trans isomer kept in vacuo. The $^{31}P-\{^{1}H\}$ n.m.r. spectra of this reaction indicated that the trans isomer was gradually converted to the fac with total conversion after a period of 48 hours. Our results are therefore consistent with those of Shaw et al [188].

The crystals of the trans isomer were purple, apparently crystallising from a clear solution. A solution of these crystals was also purple and as we have said, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum was unchanged. On standing for a few days in darkness this colour disappeared, the ^{31}P data remaining the same. Coloured solutions and crystals have been observed in similar reaction systems and whilst we suspect that only small quantities of material are involved in producing these effects, their origin is unknown. The structures of these molecules are discussed in Appendix 1.

Figure 18

X-ray Crystal Structure of fac-[$Ir(CO)Cl_3(PEt_3)_2$]

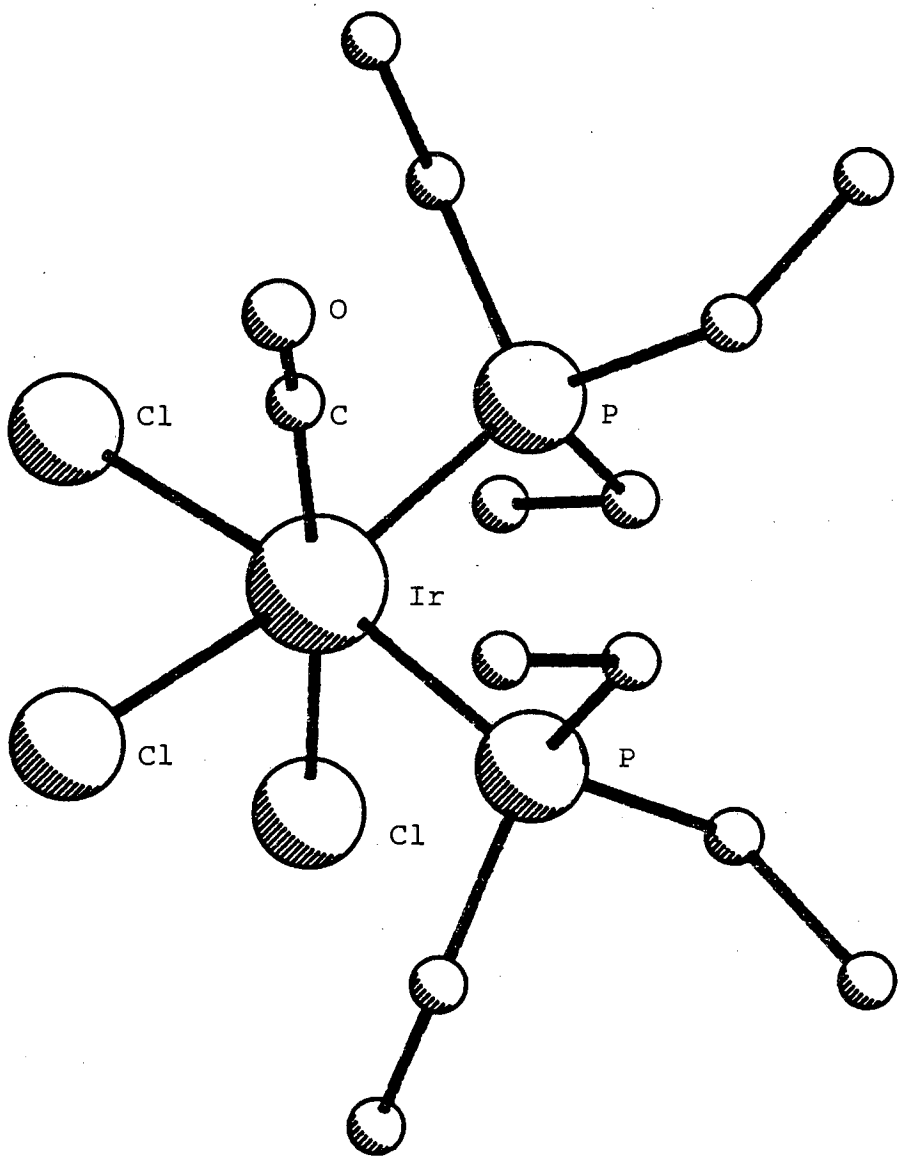
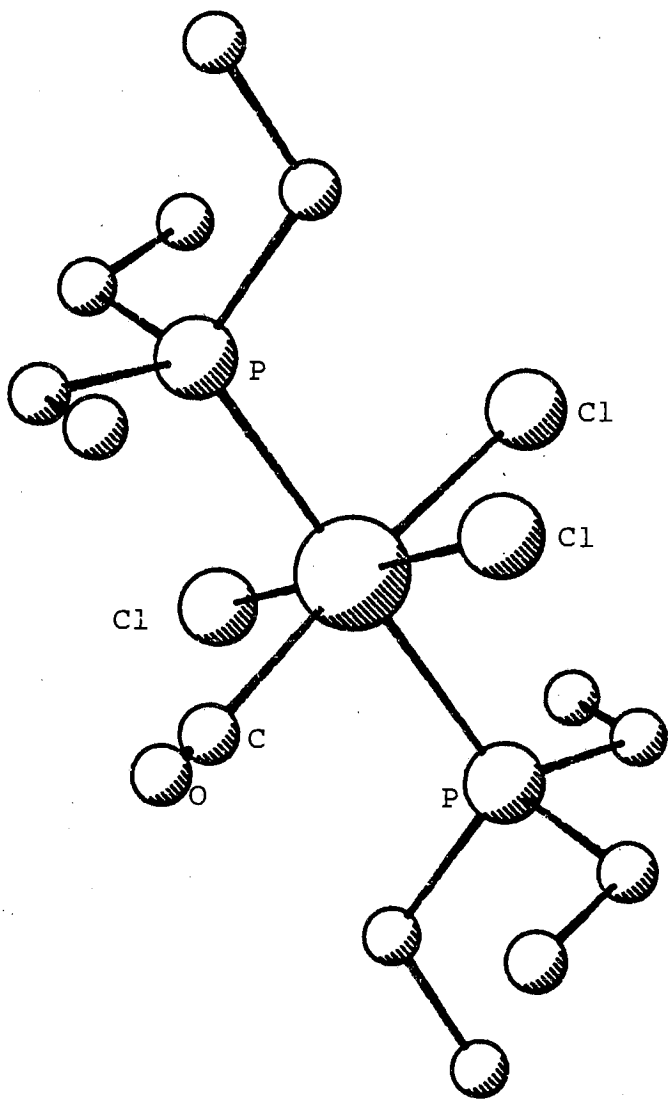


Figure 19

X-ray Crystal Structure of trans-$[Ir(CO)Cl_3(PEt_3)_2]$



Chapter 3

Some reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

The extension of previous work on the reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ [53,54] is given in this chapter. Similar reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ are given in Chapter 4. The synthesis and characterisation of $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ are also discussed along with some of its reactions.

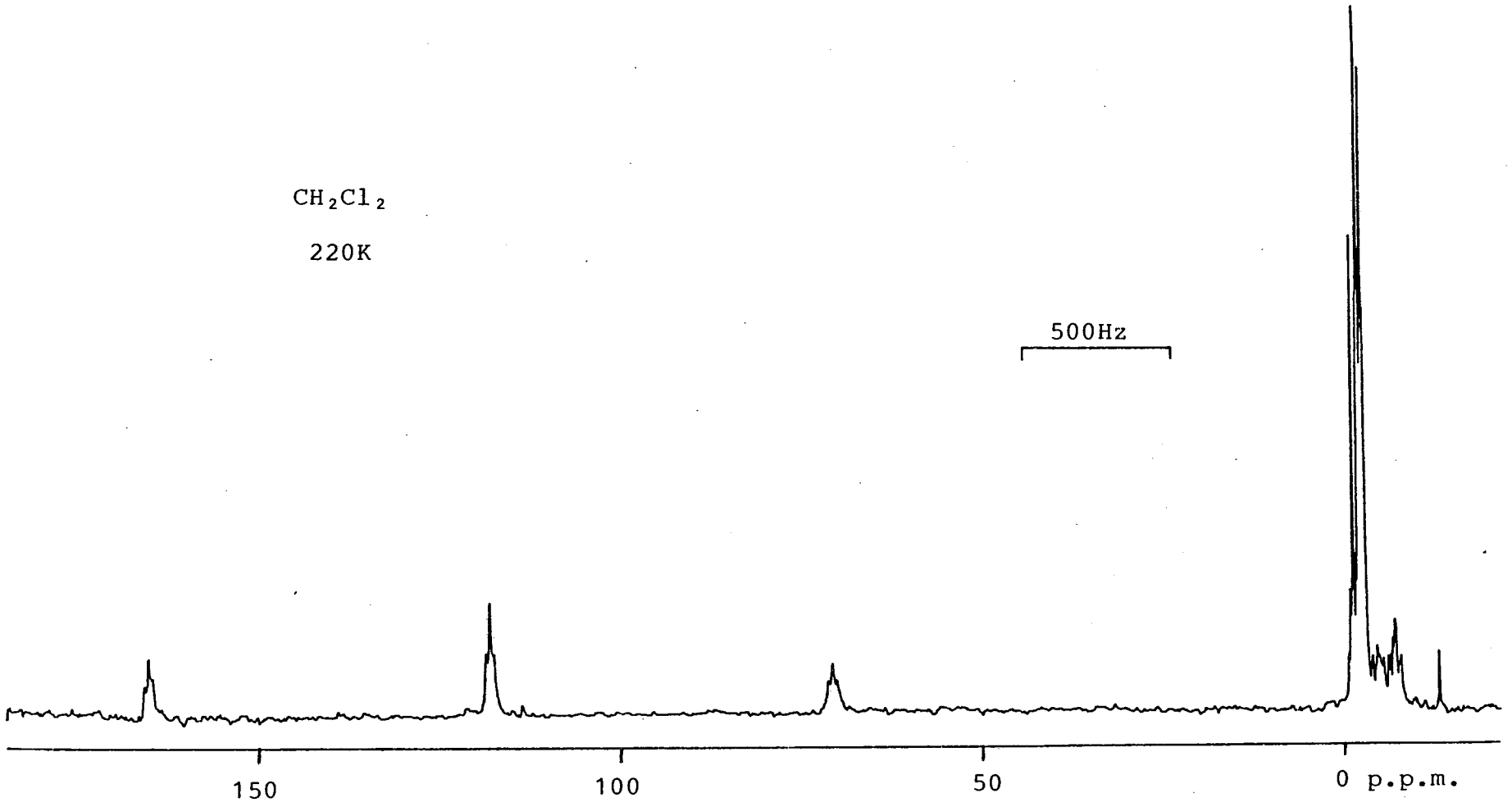
3.1 Reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$

A wide ranging study of the reactivity of this compound has already been carried out [53,54], but some reactions had been only briefly investigated namely those with dichlorine and hydrogenchloride.

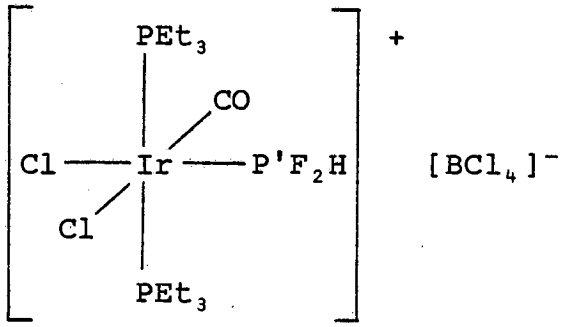
3.1(a) Hydrogenchloride

The full set of n.m.r. parameters of the product has now been obtained and the ^{31}P n.m.r. spectrum is shown in Figure 20. The ^{1}H n.m.r. spectrum appeared as a wide doublet of triplets of triplets indicating a "$P_2,P'F_2H$" system. The size of $^{1}J(P',H)$ indicates that there is a proton directly bound to the unique phosphorus. This may have been as a result of oxidative addition of hydrogenchloride to phosphorus, or by protonation of the lone pair on phosphorus. In the case of oxidative addition the product would be electrically neutral and would have a five-co-ordinated phosphorus. Addition of borontrichloride to the above species caused no change in the ^{31}P n.m.r. spectrum and the ^{11}B n.m.r. spectrum showed a sharp peak at 7.4 p.p.m. ($W_{\frac{1}{2}} \simeq 1.7$Hz), which has been assigned [167] to $[BCl_4]^-$. This shows that protonation of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ has occurred rather than addition

Figure 20 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ + HCl



of hydrogenchloride. The structure and n.m.r. parameters are given below.



$\delta P'$ = 118.2 p.p.m.		$^1J(P',F)$ = 1143 Hz	
δP = -1.8 p.p.m.		$^1J(P',H)$ = 639.1Hz	
δH = 9.17 p.p.m.		$^2J(P,P')$ = 14.0Hz	
δF = -71.6 p.p.m.		$^2J(F,H)$ = 61.0Hz	
δB = 7.4 p.p.m.		$^3J(P,H)$ = 3.0Hz	
		$^3J(P,F)$ = 4.5Hz	

All parameters were recorded in dichloromethane at 220K.

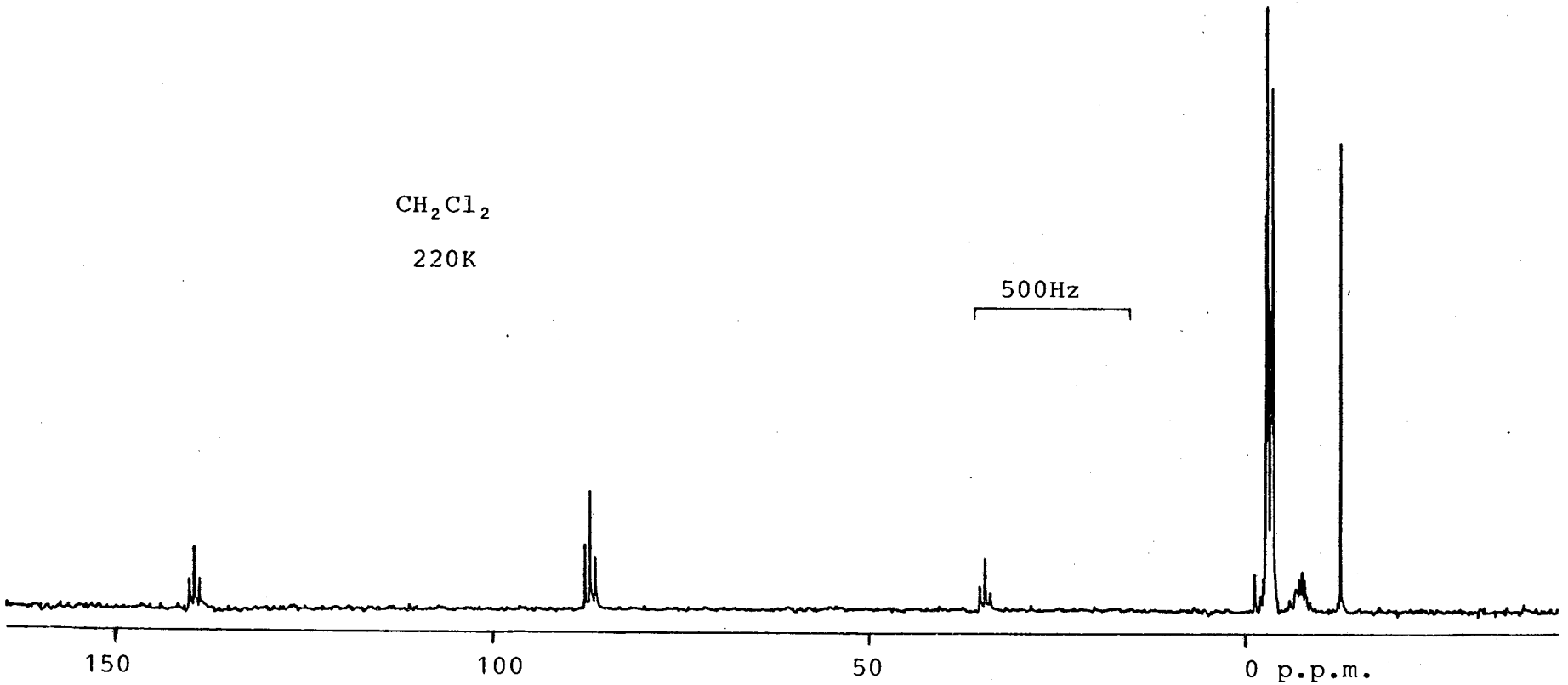
3.1(b) Dichlorine

A number of species were known to result from this reaction [53] and in a fresh investigation 1:1, 2:1 and 1:2 molar ratios of dichlorine and $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ were used.

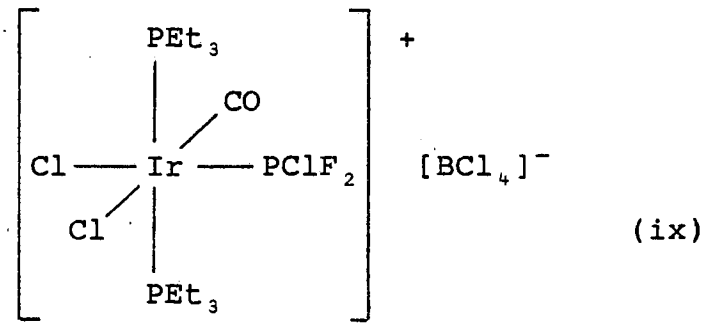
3.1(b)(i) Equimolar Reaction with Dichlorine

At 180K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed some trans-$[Ir(CO)Cl_3(PEt_3)_2]$ and one other species (ix) giving a triplet of triplets at 86.9 p.p.m. and a doublet of triplets at -2.6 p.p.m., the latter being assigned to $-PEt_3$ groups (Figure 21). In a duplicate experiment, after allowing reaction to occur at 190K, borontrichloride was added so that there were equimolar quantities of BCl_3 and (ix). There was no change in the ^{31}P n.m.r. spectrum

Figure 21 24.2MHz-^{31}P-{^{1}H}-spectrum of [Ir(CO)Cl$_2$(PEt$_3$)$_2$(PF$_2$)] + Cl$_2$



at 180K and the ^{11}B n.m.r. spectrum showed a sharp peak at 7.4 p.p.m. ($W_{\frac{1}{2}} \simeq 1Hz$) which may be assigned [167] to $[BCl_4]^-$. A ^{19}F n.m.r. spectrum was also obtained and the n.m.r. data are given in Table 1. The structure shown below is consistent with these results.

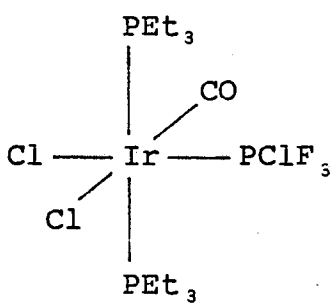


(ix)

No further reaction was observed on warming the solution to 300K.

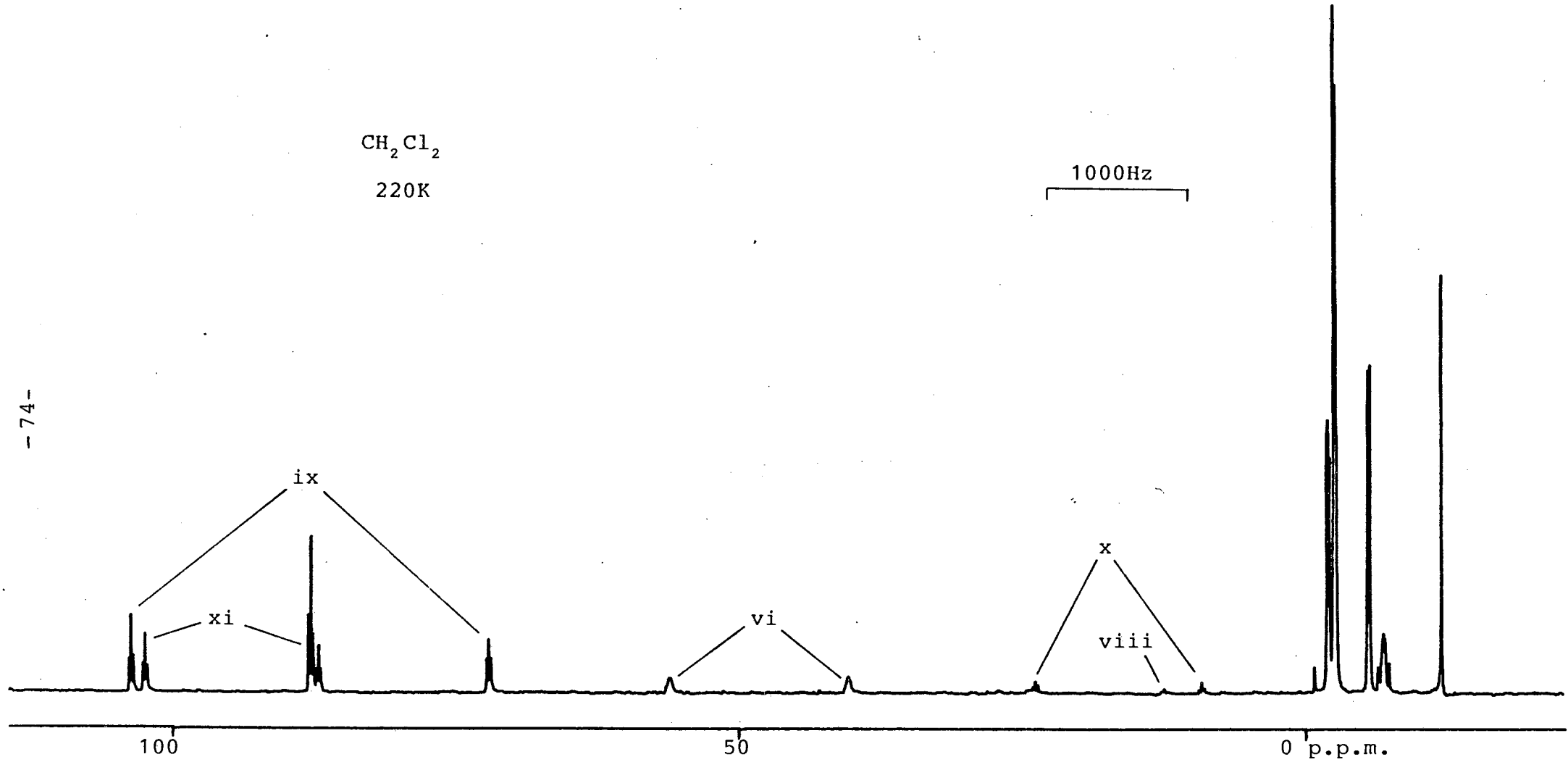
The original reaction which had taken place in the absence of borontrichloride, was now observed as the solution was warmed from 180K and at 240K further reaction occurred. According to $^{31}P-\{^1H\}$ n.m.r. data (Figure 22) resonances from (ix) were present along with resonances from four new species; (vi), (viii), (x) and (xi). Each showed the pattern expected of a "$P_2,P'F_n$" species (Table 1) and the structures can be deduced from the P-F couplings.

A quartet of triplets at 48 p.p.m. and a broad doublet at -5.6 p.p.m. are assigned to:



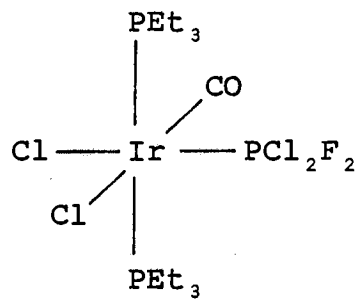
(vi)

Figure 22 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)] + Cl_2$



This species is molecular since the similar species (vii), whose spectrum showed the same multiplet patterns at different shifts, has been shown to be ionic, vid. the reaction of $[Ir(CO)Cl(PEt_3)_2]$ with PCl_2F_3 (see Sections 2.3(d) and 3.1(b)(ii)).

A triplet of triplets at 13.8 p.p.m. and a doublet of triplets at -6.6 p.p.m. are assigned to:



(viii)

in the molecular form since the species (ix), which gave similar multiplets at different shifts, has been shown to be ionic.

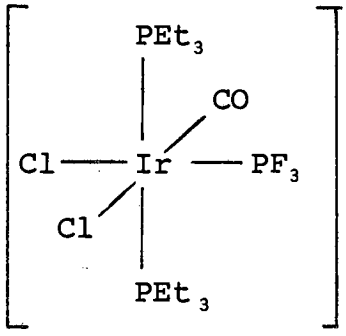
The remaining species (x) and (xi) have $^{31}P-\{^1H\}$ n.m.r. spectra as follows: a doublet of triplets at 16.7 p.p.m. and a doublet of doublets at -6.8 p.p.m. (x), and the same spin system at 95 and -2 p.p.m. respectively (xi). These are believed to be the molecular and ionic forms of $[Ir(CO)Cl_2(PEt_3)_2(PCl_3F)]$, and we were able to distinguish these later (see Section 4.1(h)).

Some of the resonances namely (viii) and (x) were of low intensity, so the n.m.r. data (Table 1) and the assignments must be regarded as tentative for these species. However we do not feel that hydrolysis occurred since we know the parameters for $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PF_2O)]$. The species

$[Ir(CO)Cl_2(PEt_3)_2(PClFO)]$ for which we have no parameters is unlikely to have been produced, since the presence of a chiral phosphorus atom would cause more complex splitting patterns than are seen here. We also note here that the removal of Cl^- by BCl_3 addition prevented further reaction of the species (ix).

3.1(b)(ii) Reaction with a 2:1 Molar Excess of Dichlorine

As with previous stoichiometry this reaction produces (ix) alone at 180K and reacts further at 240K. The $^{31}P-\{^1H\}$ n.m.r. spectrum then showed four species, (ix), (vii), (x) and (xi) (see Figure 23). The spectrum of the new species (vii) consisted of a quartet of triplets at 58 p.p.m. and a doublet of quartets at -0.9 p.p.m.. This was assigned to



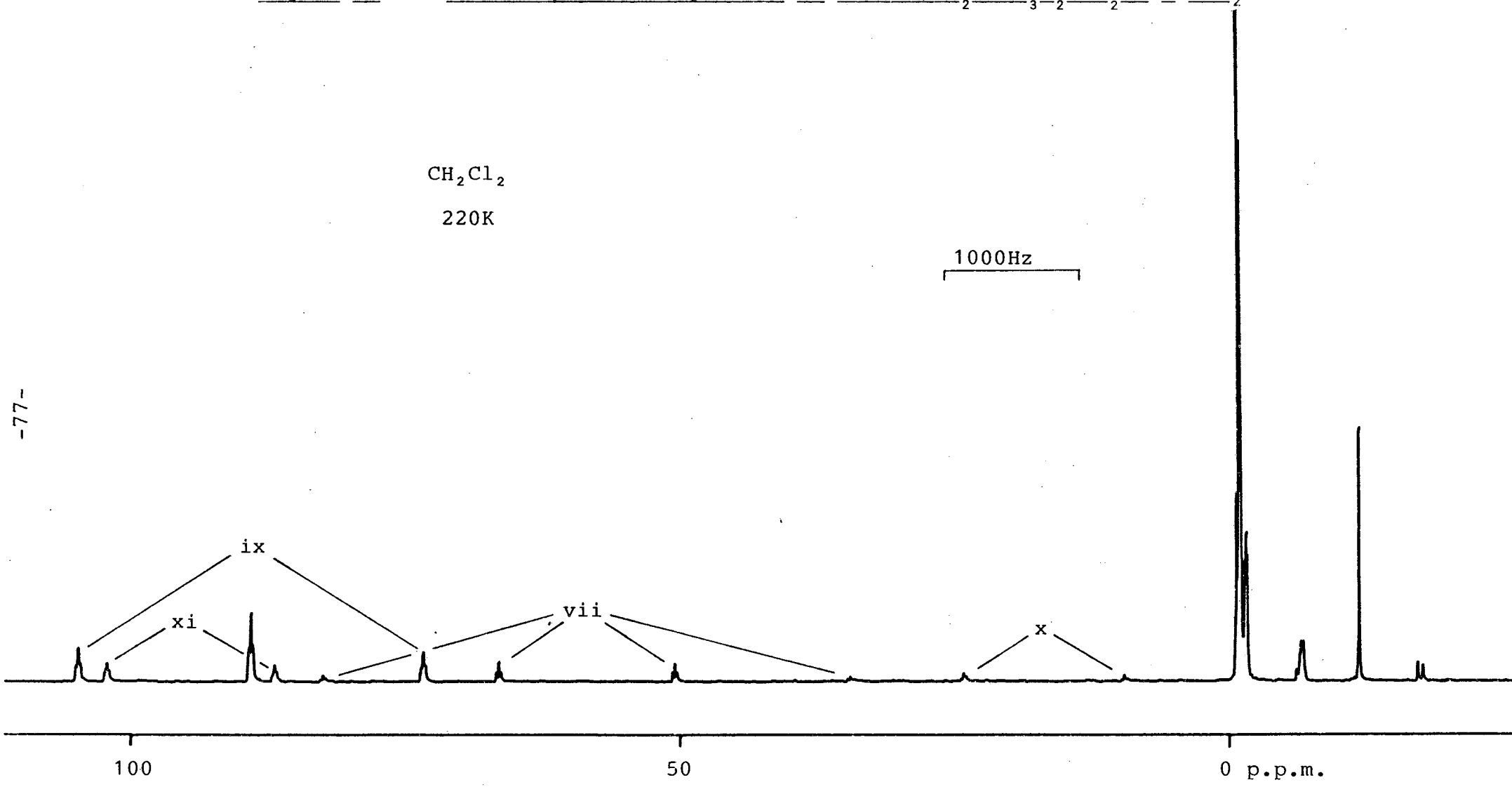
(vii)

and is the same as the species obtained by the reaction of PCl_2F_3 with $[Ir(CO)Cl(PEt_3)_2]$ (see Section 2.3(d)). The other species have been discussed previously. The n.m.r. data are given in Table 1.

3.1(b)(iii) Reaction with a 2:1 Molar Excess of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$

Some unreacted $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ is present at 180K, along with (ix). On warming to 220K, further reaction occurred. The $^{31}P-\{^1H\}$ n.m.r. spectrum

Figure 23 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)] + 2Cl_2$



at this temperature showed eight species (Figure 24): $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ (i) was still present, but (ix) was not; $[Ir(CO)Cl_2(PEt_3)_2(PFCl)]$ (ii) was identified [53], as were $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ (iii), (vi), (viii), PCl_3 and PF_3. The eighth compound had a ^{31}P n.m.r. spectrum which comprised a quintet of triplets at -72 p.p.m. and a doublet of quintets at -9.8 p.p.m.. This was identified as the novel complex $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ (iv), the first metal $-PF_4$ complex to be reported, which is discussed in Section 3.1(d). The n.m.r. data are in Table 1.

It is worth noting here that the ^{31}P chemical shifts of both the -P' and $-PEt_3$ groups varied by up to 2 p.p.m. depending on the stoichiometry of the reaction. Since the spin system and coupling constants remained the same, this does not bring the identity of the compounds into doubt.

A comparison of the species formed in the reactions of excess metal complex and excess dichlorine is also interesting. The products in the reaction with excess dichlorine were mainly ionic, the exception being (x) which contained a $-PCl_3F$ group (see Section 4.1(h)). In contrast, all the species formed in the reaction with excess metal complex were molecular. The suggestion that formation of the Cl_3^- ion is favoured and that ionisation of any molecular species is caused by dichlorine is consistent with these observations.

Figure 24 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)] + \frac{1}{2}Cl_2$

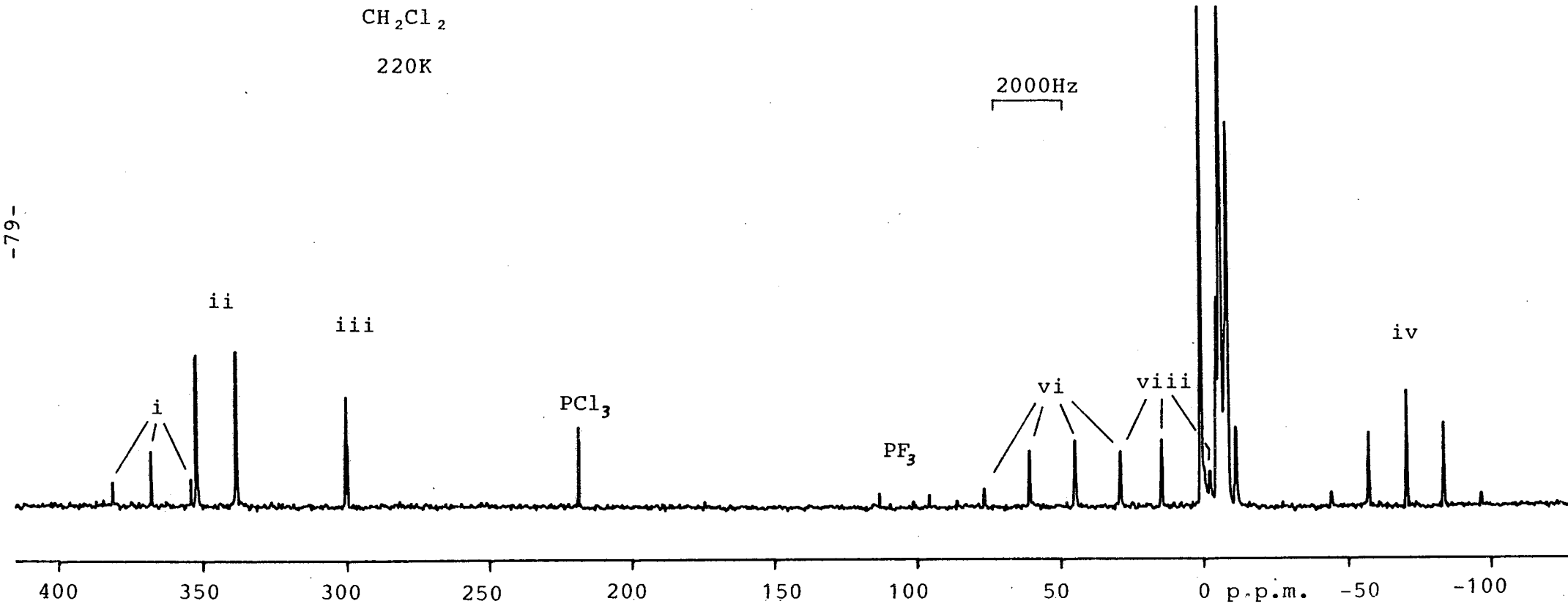


Table 1 N.m.r. Parameters for the Products of the Reaction of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ with Dichlorine

Compound		$\delta P'$	δP	δF	δB	$^2J(P,P')$	$^1J(P',F)$	$^3J(P,F)$
$[Ir(CO)Cl_2(PEt_3)_2(P'F_2)]$	(i)	364.8	-9.3	-68.3	-	9.2	1105	11.6
$[Ir(CO)Cl_2(PEt_3)_2(P'ClF)]$	(ii)	345.2	{ -6.8 / -10.6 }	-106.1	-	{ 4 / 31 }	1121	22
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$	(iii)	304.0	-9.2	-	-	34.0	-	-
$[Ir(CO)Cl_2(PEt_3)_2(P'F_4)]$	(iv)	-72.0	-9.82	-0.20	-	22.6	1062	5.8
$[Ir(CO)Cl_2(PEt_3)_2(P'ClF_3)]$	(vi)	48.1	-5.59	-25.0	-	18.2	1292	2.3
$[Ir(CO)Cl_2(PEt_3)_2(P'F_3)][BCl_4]$	(vii)	58.4	-0.87	-25.0	7.4	17.9	1302	2.5
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2F_2)]$	(viii)	13.8	-6.56	-13.5	-	19.5	1186	3.4
$[Ir(CO)Cl_2(PEt_3)_2(P'ClF_2)][BCl_4]$	(ix)	87.9	-2.61	-15.6	7.4	16.2	1276	4.1
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_3F)]$	(x)	16.7	-6.76	+11.1	-	16.7	1189	5.6
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2F)][BCl_4]$	(xi)	94.8	-2.02	-12.5	a	14.8	1229	8.9

Chemical shifts are given in p.p.m. and coupling constants in Hz.
All parameters were recorded in dichloromethane at 220K.
a See text.

3.1(c) Phosphoruspentafluoride

This reaction is not understood and we shall briefly report the results here. An equimolar mixture of PF_5 and $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ in either toluene or dichloromethane was observed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. At 180K no reaction had occurred, but at 200K $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ (sic) was present. There were also multiplets at about 180 and -144 p.p.m., and a singlet at -8 p.p.m., but we do not know from what species these arise. By 210K the $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ had disappeared and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ was the major product (Figure 25). We were unable to study this reaction any further. The chloride may have come from other iridium complexes in solution, but in any case the reaction here was not as simple as that between $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and PCl_5 (see Section 4.1(i)).

3.1(d) Xenondifluoride [190]

The use of xenondifluoride as a mild fluorinating agent has been noted by Holloway et al [191]. We therefore attempted the reaction of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ with XeF_2. At 280K or above, reaction was rapid, the reaction mixture bubbling vigorously, presumably as xenon gas was produced. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the resulting solution showed a single species, consisting of a quintet of triplets at -72.9 p.p.m. (Figure 26) and a doublet of quintets at -9.87 p.p.m. (Figure 27). The ^{19}F spectrum was sharp at 300K, showing a wide doublet of triplets, but this became

Figure 25 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)] + PF_5$

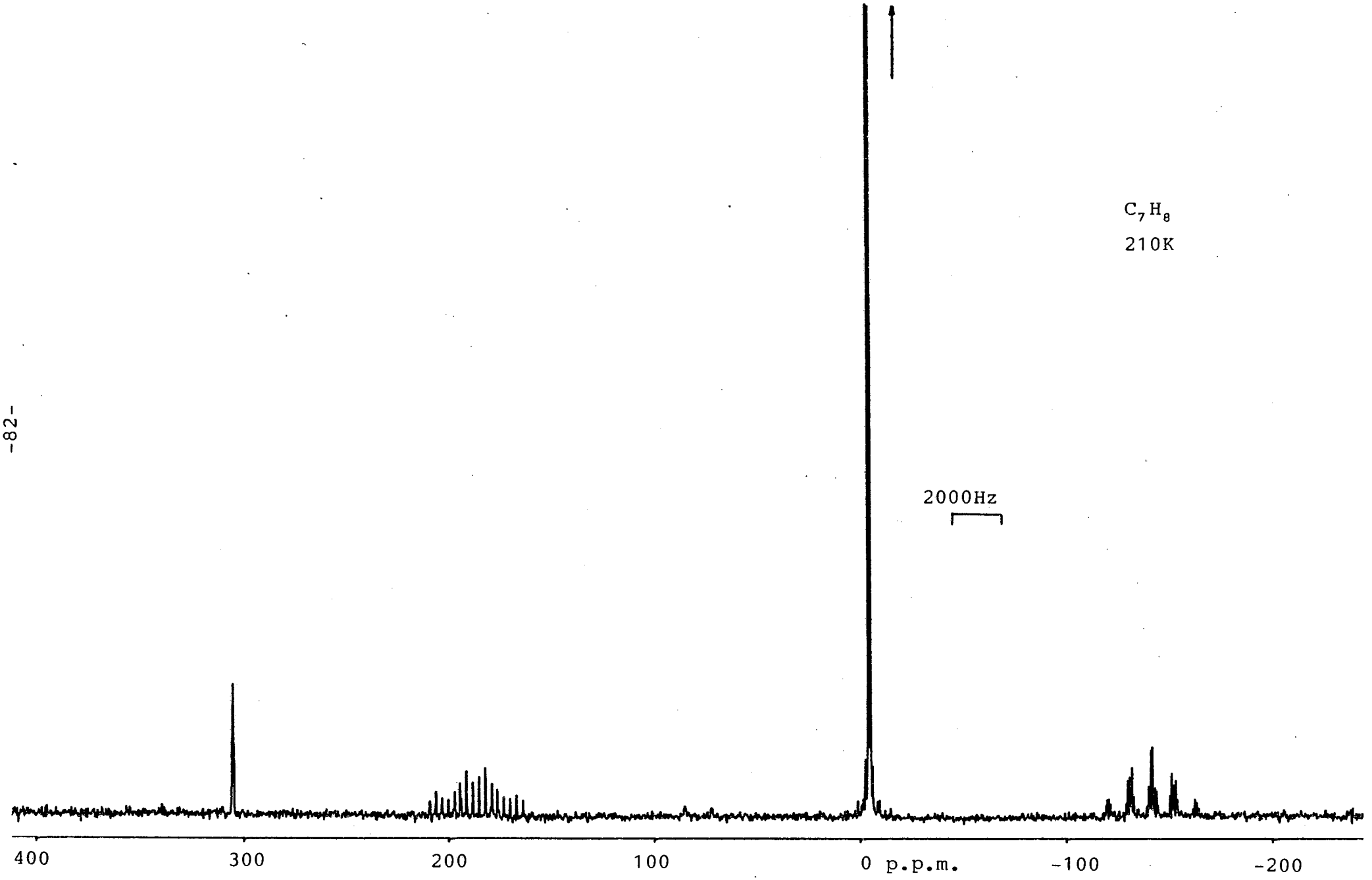


Figure 26 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

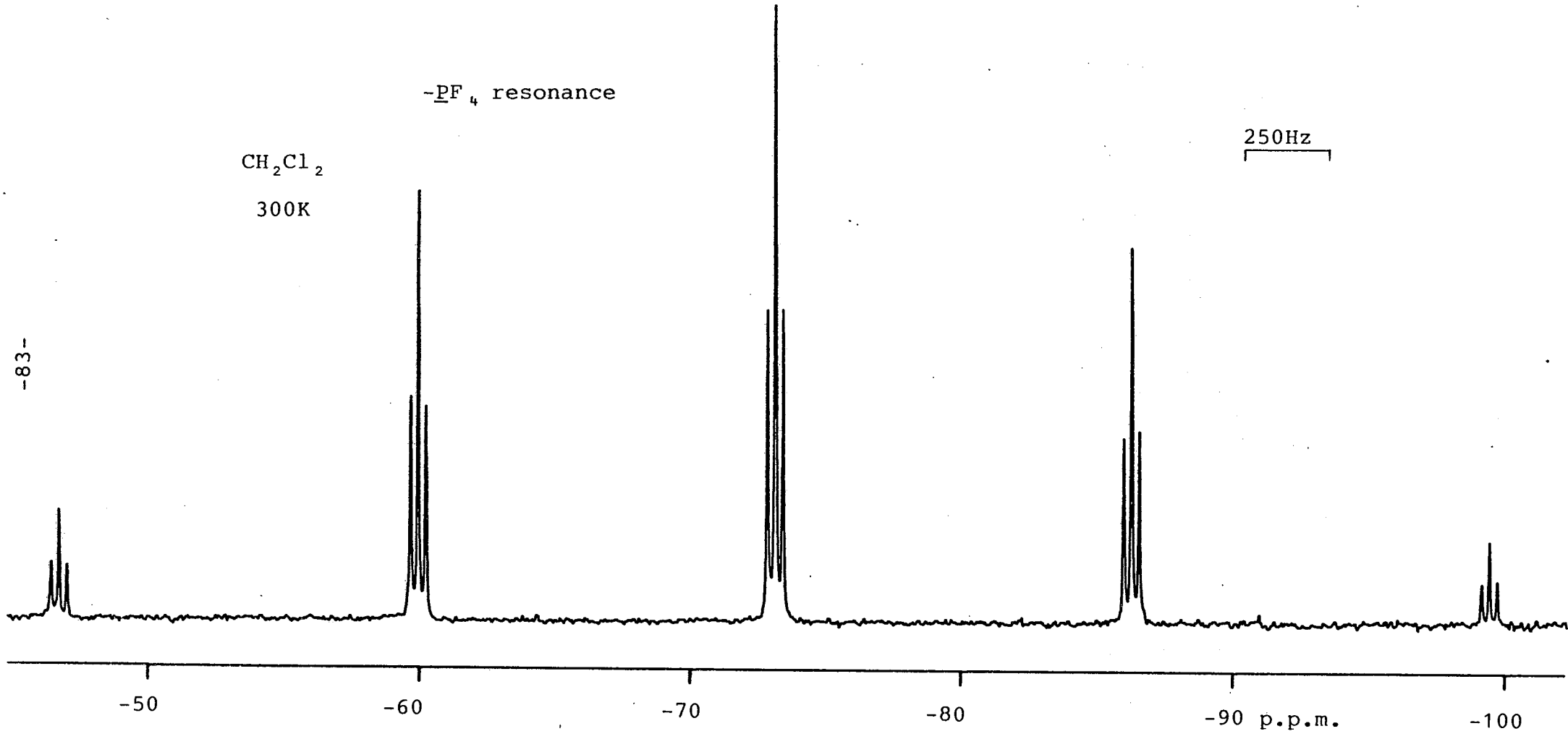
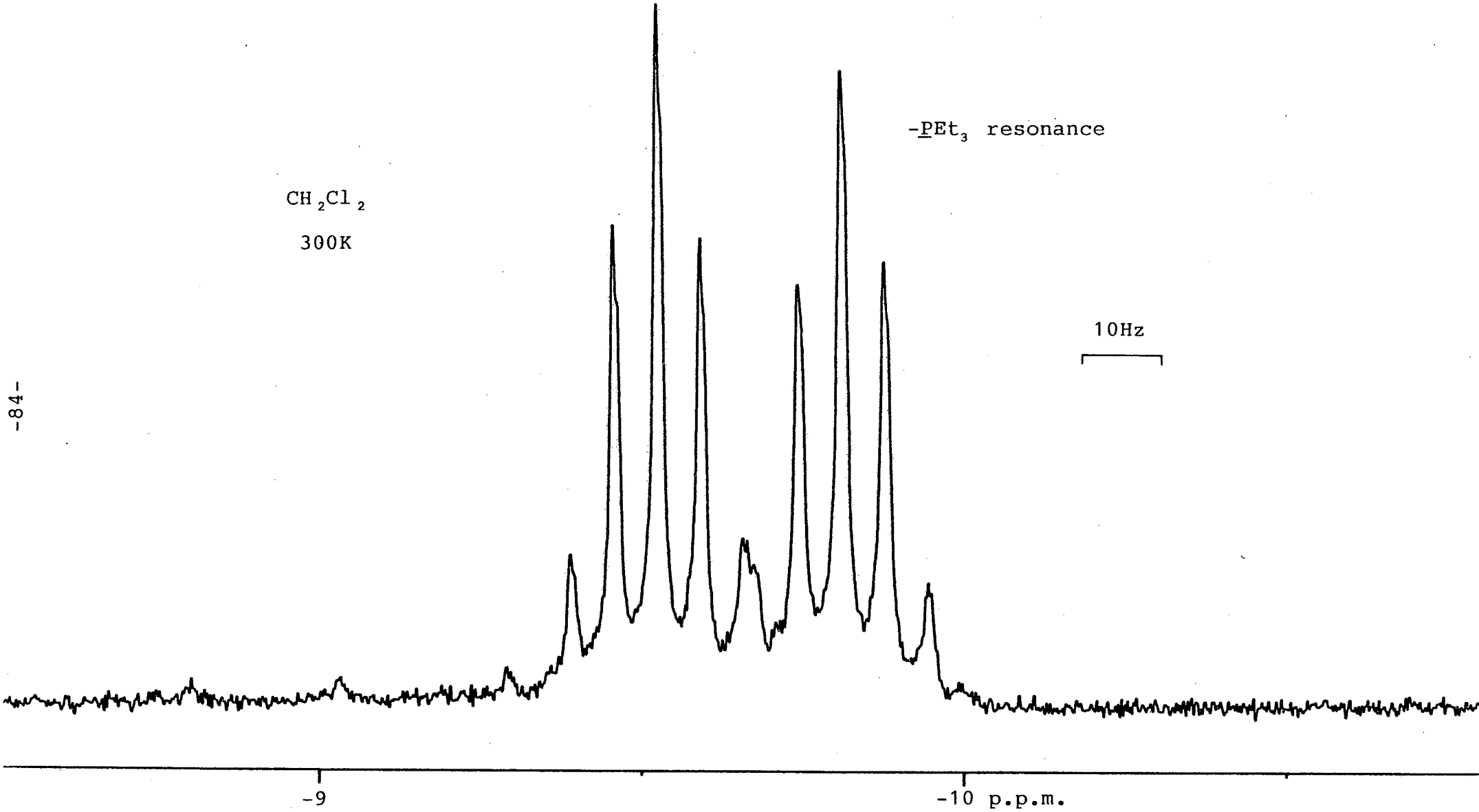
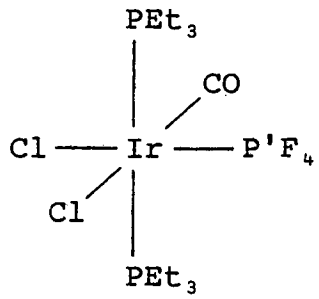


Figure 27 81.0MHz-^{31}P-{^{1}H}-spectrum of [$Ir(CO)Cl_2(PEt_3)_2(PF_4)$]



broad at 190K, although the phosphorus coupling was retained. We believe that the species is $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ (iv) whose structure and n.m.r. parameters are given below.



(iv)

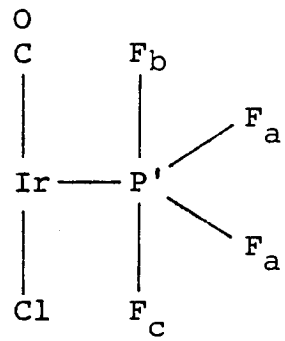
$\delta P'$ = -72.9 p.p.m. $^1J(P',F)$ = 1062 Hz

δP = -9.87 p.p.m. $^2J(P,P')$ = 22.6Hz

δF = -0.20 p.p.m. $^3J(P,F)$ = 5.8Hz

Parameters were recorded at 220K in dichloromethane.

On cooling an ether / dichloromethane solution to 130K, the ^{19}F n.m.r. spectrum showed that there were three different fluorine sites in the molecule [192] (Figure 28). These were made equivalent by allowing the system to warm, coalescence occurring at 145K. Integration showed that the three different sites were in the rough ratio 1:1:2, the resonance representing two fluorines having $^1J(P',F)$ = 1088Hz. Since this is the largest of the PF couplings, these fluorines are equatorial. This implies that the stereochemistry at P' is as follows:



δF_a = -43.57 p.p.m. $^1J(P',F_a)$ = 1088Hz

δF_b = 33.17 p.p.m. $^1J(P',F_b)$ = 975Hz

δF_c = 57.90 p.p.m. $^1J(P',F_c)$ = 922Hz

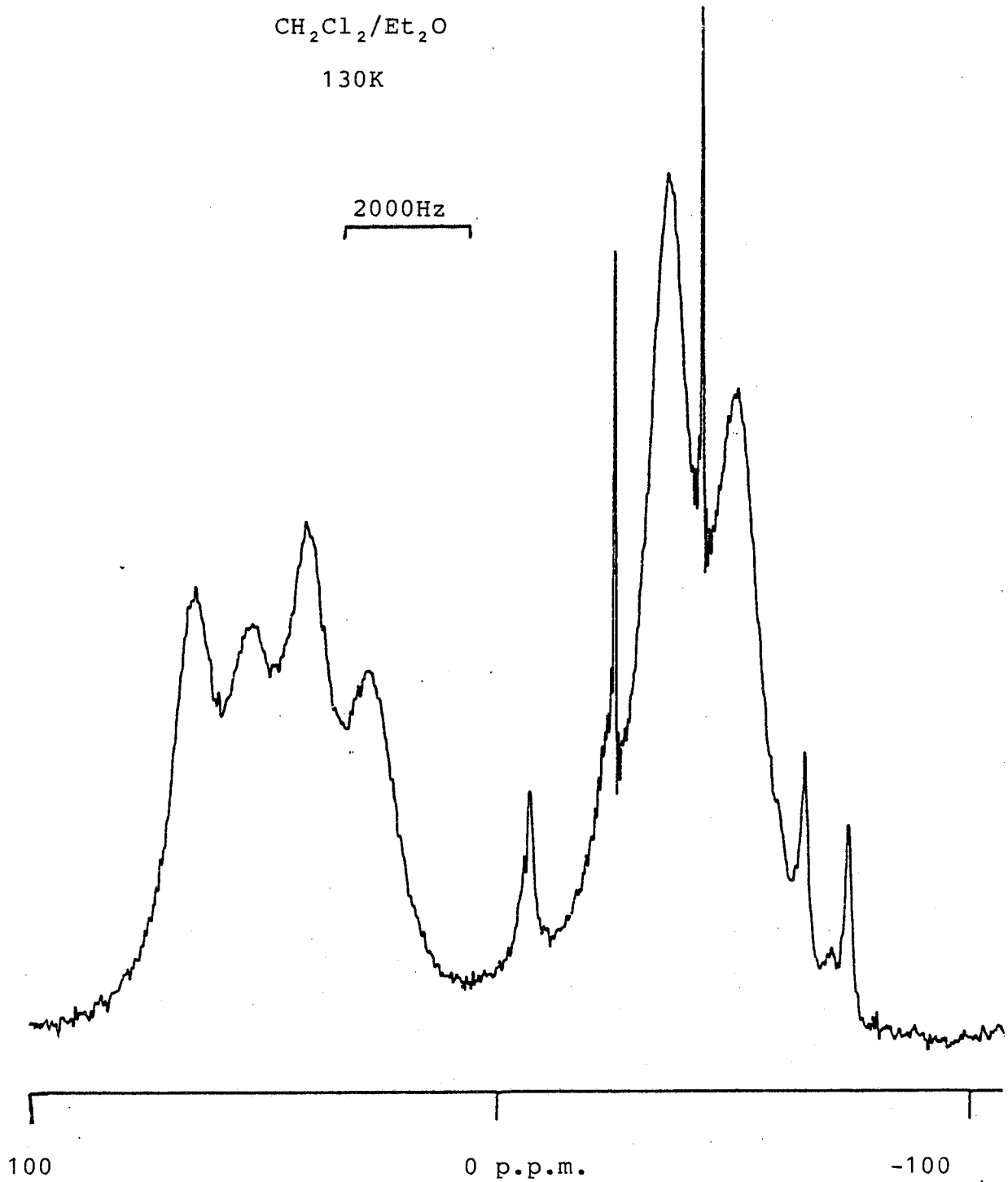
Parameters were recorded at 130K in a 2:1 diethylether / dichloromethane mixture.

The chemical inequivalence of the axial fluorines may be because the rotation around the Ir-P bond has slowed. This may mean that F_b and F_c are in the Cl-Ir-CO plane. The exchange process must consist of permutation of the axial and equatorial sites as well as permutation of the two axial sites. A Berry pseudorotation process would exchange the axial and equatorial sites and rotation about the Ir-P' bond would exchange the axial positions. Both these processes must be occurring simultaneously, because there is only one coalescence temperature [193].

In an attempt to calculate the activation energy for the fluxional process we averaged the chemical shift values for F_b and F_c and used the chemical shift difference between the non-coalesced absorption maxima to obtain a value of 46kJ mol^{-1} [194], which is close to the value obtained from a study of $PF_4(SCH_3)$ by Cavell et al [193].

Figure 28

75.4MHz-^{19}F-spectrum of [Ir(CO)Cl$_2$(PEt$_3$)$_2$(PF$_4$)]



3.2 Reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

The reactivity of the above compound was briefly investigated. In contrast to PF_5, there was no reaction with NMe_3 according to ^{31}P and ^{19}F n.m.r. spectra [195].

3.2(a) Water

This reaction was investigated using $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Reaction occurred at 300K to give $[Ir(CO)Cl_2(PEt_3)_2(PF_2O)]$, which has been characterised elsewhere [53,54].

3.2(b) Phosphoruspentafluoride

The $^{31}P-\{^1H\}$ n.m.r. spectrum of the solution at 180K shows no reaction, but at 190K, reaction occurred to give $[Ir(CO)Cl_2(PEt_3)_2(PF_3)]^+$ (vii) and $[PF_6]^-$.

Chapter 4

Some reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$

This chapter contains details of reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$, of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ and of a compound (v) isolated from the reaction of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with dichlorine. We also include a discussion which attempts to link some of the observations made in this thesis.

4.1 Reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$

Some reactions of this compound have already been reported [53,56] and an extension of this work is now given.

4.1(a) Borontrichloride

Reactions with the boron halides BF_3 and BCl_3 were both investigated; BF_3 showed no reaction after prolonged standing at 300K, but BCl_3 reacted at low temperature. The $^{31}P-\{^1H\}$ n.m.r. spectrum at 190K showed a 1:1:1:1 quartet at 128 p.p.m. ($W_{\frac{1}{2}} \simeq 120Hz$) and a doublet at -6.6 p.p.m. (Figure 29). The ^{11}B n.m.r. spectrum showed only a single resonance: a broad doublet, $^1J(P',B) = 137Hz$ ($W_{\frac{1}{2}} \simeq 50Hz$). The structure shown below is consistent with these results.

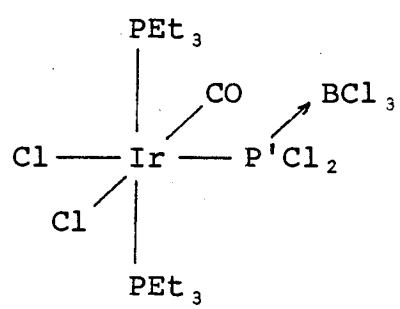
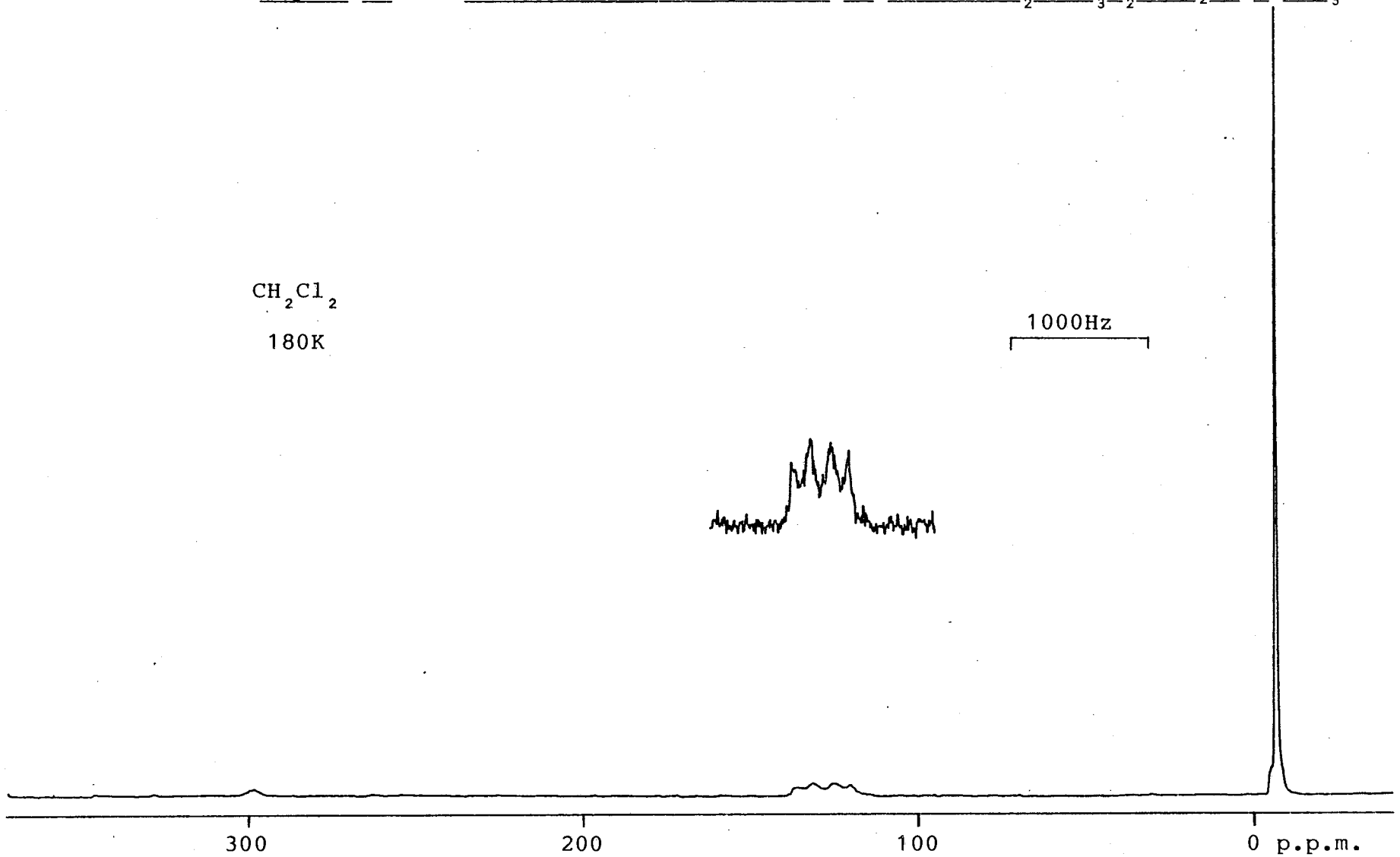


Figure 29 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ + BCl_3



$\delta P' = 127.8$ p.p.m. $\quad {}^1J(P',B) = 137$ Hz

$\delta P = -6.6$ p.p.m. $\quad {}^2J(P,P') = 6.1$Hz

$\delta B = 7.0$ p.p.m.

All parameters were recorded in dichloromethane at 190K

4.1(b) Diborane

The reaction between $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and B_2H_6 in a 2:1 molar ratio was examined by $^{31}P-\{^1H\}$ n.m.r. spectroscopy which showed, at 180K a broad singlet at 190 p.p.m. ($W_{\frac{1}{2}} \simeq 50$Hz), assigned to P', and a sharp doublet from the $-PEt_3$ groups at -9 p.p.m. (Figure 30). The $^{11}B-\{^1H\}$ n.m.r. spectrum at 270K showed a broad peak ($W_{\frac{1}{2}} \simeq 100$Hz), in which no splitting could be resolved. Upon retention of proton coupling, a quartet pattern ($^1J(B,H) = 100$Hz) was observed. In the ^1H n.m.r. spectrum a broad featureless hump ($W_{\frac{1}{2}} \simeq 20$Hz) was enhanced by irradiating ^{11}B, and this was assigned to the BH protons. The structure below is consistent with these results. The compound decomposed above 270K.

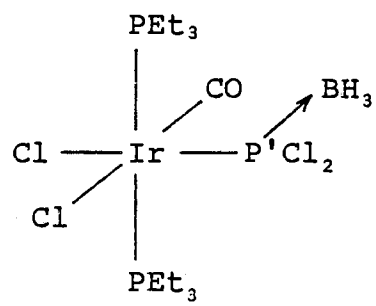
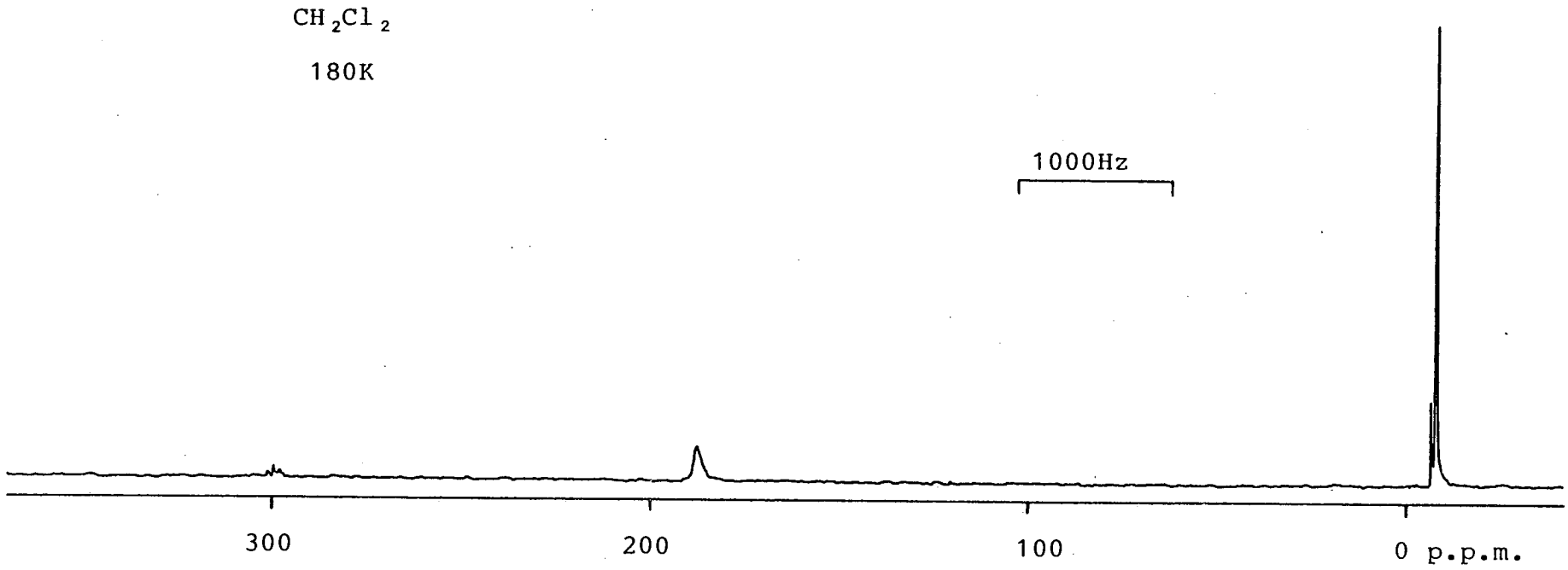


Figure 30 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ + $\frac{1}{2}B_2H_6$



$\delta P' = 190.1$ p.p.m. $^1J(B,H) = 100$ Hz

$\delta P = -9.0$ p.p.m. $^1J(P',B)$ not resolved

$\delta H = 2.0$ p.p.m. $^2J(P,P') = 4.55$Hz

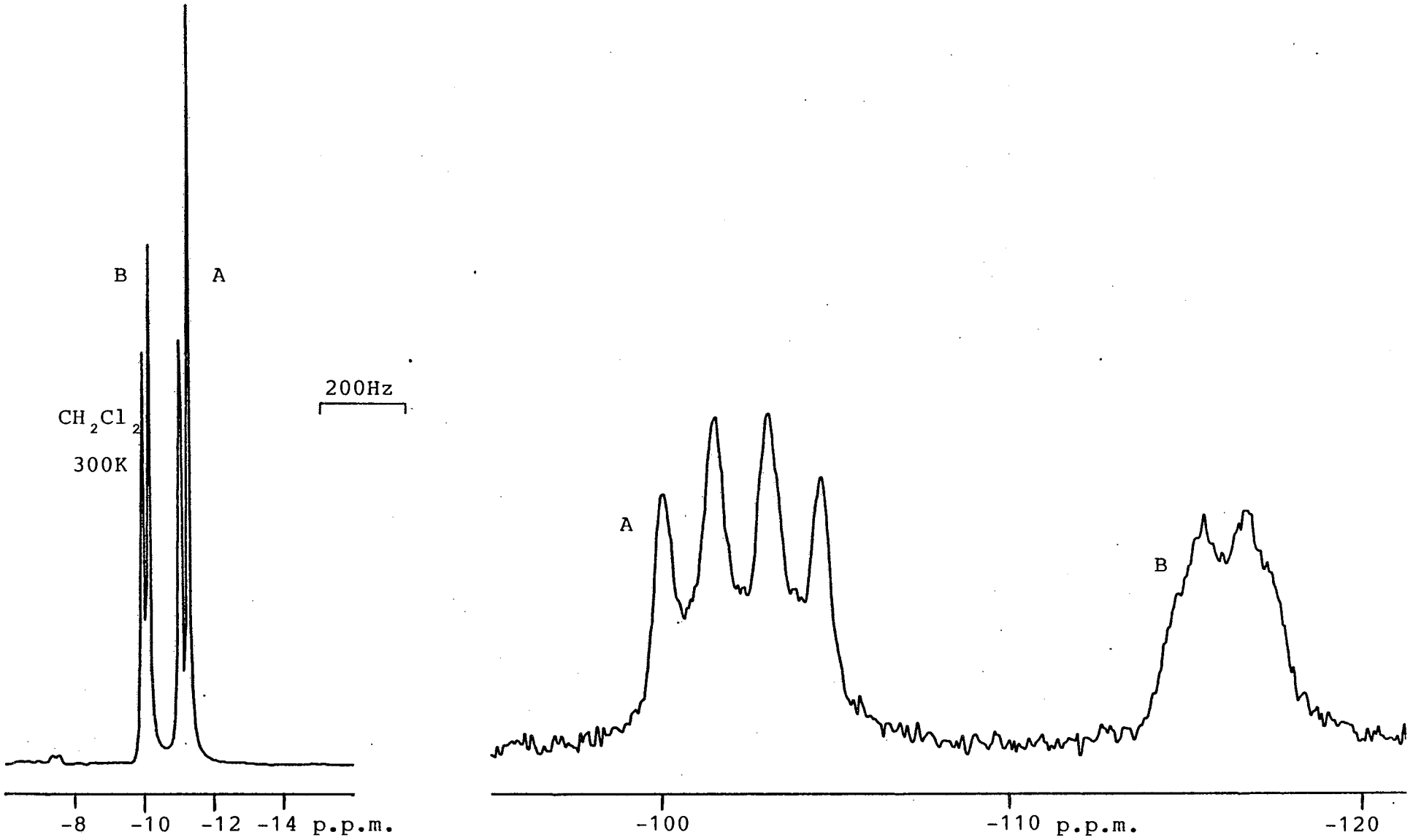
$\delta B = -9.1$ p.p.m.

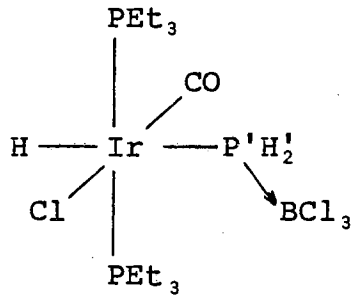
All the parameters were recorded in dichloromethane at 270K.

Reaction between equimolar amounts of B_2H_6 and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ was not as simple. The initial product was the same as above but this decomposed above 270K. At 300K there were two products (A) and (B), which could be identified by their n.m.r. spectra (Figure 31). Slightly more of species (A) had been formed than of species (B) and the $-PEt_3$ and P' resonances were related by examination of a proton-coupled ^{31}P n.m.r. spectrum.

The formulation of one product was $[Ir(CO)ClH(PEt_3)_2\{P'H'_2(BCl_3)\}]$ (A). A broad 1:1:1:1 quartet at -102 p.p.m. was assigned as P' ($W_{\frac{1}{2}} \simeq 80$Hz), and this was then split further into a 1:2:1 triplet, $^1J(P',H) = 350$Hz, on retention of proton coupling. The ^1H n.m.r. spectrum contained P'H' and IrH resonances in the ratio 2:1. The values of $^2J(P,H)$ and δ(IrH) showed that H must be <u>trans</u> to P'. The $^{11}B-\{^1H\}$ n.m.r. spectrum showed a doublet ($W_{\frac{1}{2}} \simeq 30$Hz) at 4.3 p.p.m., which was unchanged on coupling the protons. The structure and n.m.r. parameters of (A) are given below.

Figure 31 80.1MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ + B_2H_6





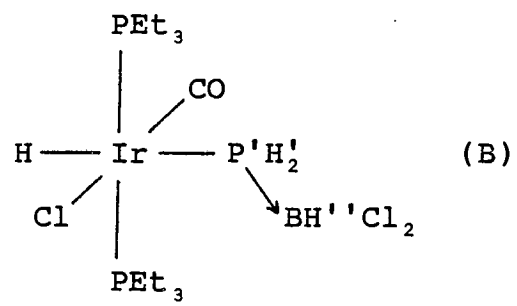
(A)

$\delta P'$ =	-102.4 p.p.m.	$^1J(P',H')$ =	333.2Hz
δP =	-11.13 p.p.m.	$^1J(P',B)$ =	126 Hz
δH =	-8.76 p.p.m.	$^2J(P,P')$ =	19.1Hz
$\delta H'$ =	+3.84 p.p.m.	$^2J(P',H)$ =	138.0Hz
δB =	+4.3 p.p.m.	$^2J(P,H)$ =	13.1Hz
		$^3J(P,H')$ =	5.7Hz

All the parameters were recorded in dichloromethane at 300K.

The other product was $[Ir(CO)ClH(PEt_3)_2\{P'H'_2(BH''Cl_2)\}]$ (B), which had a broad P' resonance ($W_{\frac{1}{2}} \simeq 130$Hz) at -116 p.p.m., showing a 1:1:1:1 quartet structure (Figure 31). In a similar manner to (A), this resonance split further when the protons were coupled, showing that the P' was coupled to two equivalent protons ($^1J(P',H') \simeq 350$Hz). The ^1H n.m.r. spectrum showed that the P'H' and IrH resonances were in the ratio of 2:1. When the ^1H n.m.r. spectrum was observed whilst irradiating ^{11}B, a broad doublet ($W_{\frac{1}{2}} \simeq 30$Hz) was enhanced and was assigned to the BH proton [$^2J(P',H'') = 24$Hz at 4 p.p.m.]. The $^{11}B-\{^1H\}$ resonance

($W_{\frac{1}{2}} \simeq 80Hz$) was a doublet ($^1J(P',B) = 87Hz$) and split into a further doublet ($^1J(B,H'') = 142Hz$) when proton coupling was restored. The chemical shift of the hydride and its coupling constant to P' indicated that it was <u>trans</u> to P'. The structure and n.m.r. parameters of (B) are given below.



(B)

$\delta P'$ = -116.4 p.p.m.		$^1J(P',H')$ = 325.4Hz	
		$^1J(P',B)$ = 87 Hz	
δP = -10.03 p.p.m.		$^1J(B,H'')$ = 142 Hz	
δH = -8.66 p.p.m.		$^2J(P,P')$ = 15.1Hz	
		$^2J(P',H)$ = 131.2Hz	
$\delta H'$ = +3.44 p.p.m.		$^2J(P,H)$ = 13.2Hz	
		$^2J(P',H'')$ = 24 Hz	
$\delta H''$ = +4.03 p.p.m.		$^3J(P,H')$ = 5.6Hz	
δB = -2.95 p.p.m.		$^3J(H',H'')$ = 4.2Hz	

All the parameters were obtained in dichloromethane at 300K.

<u>4.1(c) Reactions with Metal Substrates</u>

Examination of the $^{31}P-\{^1H\}$ n.m.r. spectra of solutions containing $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and either $[Pt(cod)Cl_2]$ or $[\{RuCl_2(p\text{-cymene})\}_2]$ showed that no

reaction occurred over a period of weeks at 300K. We also attempted to add dihydrogen to $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ by reaction with $[PtCl_2H_2(PEt_3)_2]$ but no reaction was observed.

4.1(d) Dinitrogentetroxide

The reaction of dioxygen with $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ slowly produces $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ but the reaction with N_2O_4 is much faster. The product was identified by partial elemental analysis, by X-ray crystallography [56] (Figure 32) and by its mass and n.m.r. spectra, the last of these being an AB_2 pattern [196] in a 24MHz-^{31}P-$\{^1H\}$ n.m.r. spectrum (Figure 33). A volatile and condensable product of the reaction was identified [197] as N_2O by its infra-red spectrum. Some non-condensable gas, which may be dinitrogen or nitrogenmonoxide, was also released during the reaction. The n.m.r. parameters of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ are given in Table 3, and the structure is discussed in Appendix 1. Some reactions of this species are discussed in Section 4.3.

4.1(e) Selenium

The reaction between Se_8 and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ has been investigated previously [53], but the ^{77}Se n.m.r. spectrum has now been obtained showing a doublet at 581 p.p.m.. This confirms the identity of the species as $[Ir(CO)Cl_2(PEt_3)_2(PCl_2Se)]$ and the n.m.r. parameters of this compound and its sulphur analogue [53] are given in Table 3.

Figure 32

X-ray Crystal Structure of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$

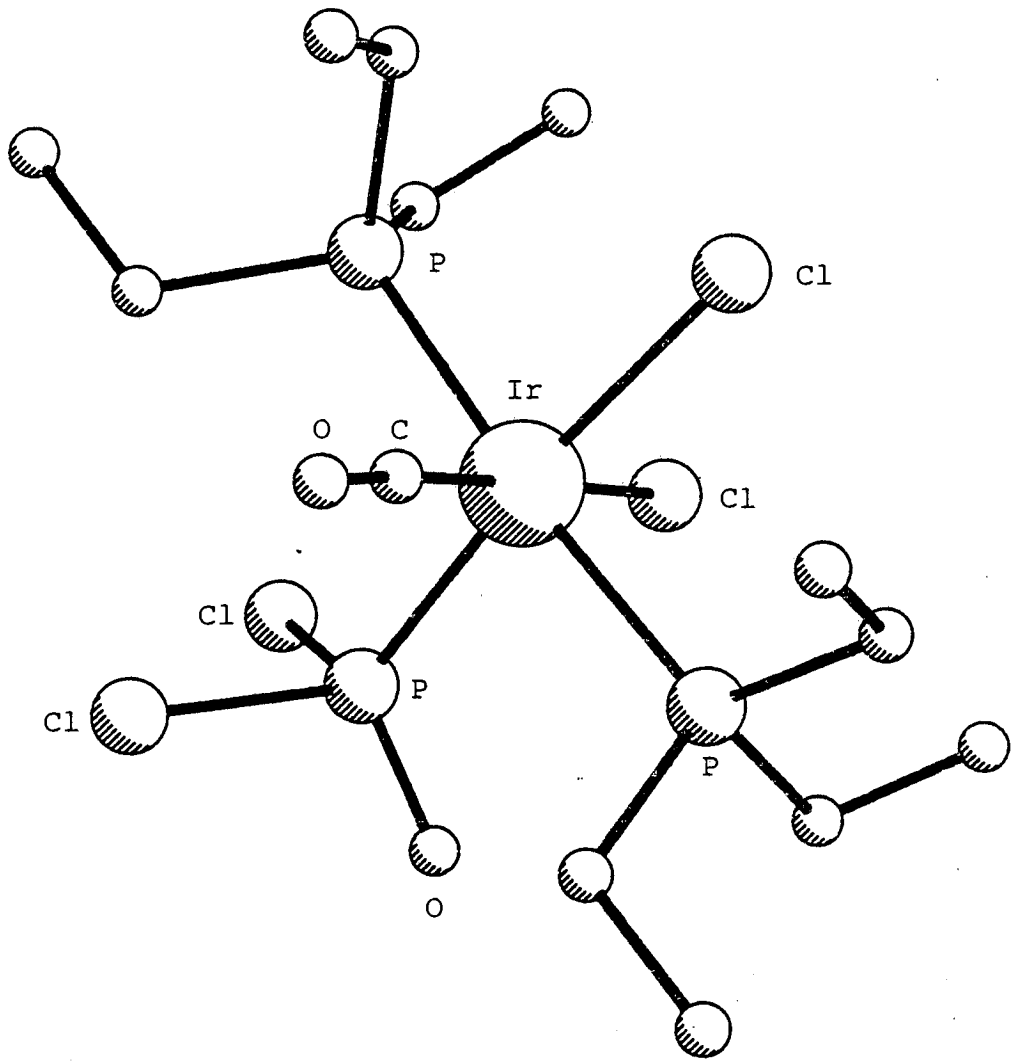


Figure 33 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$

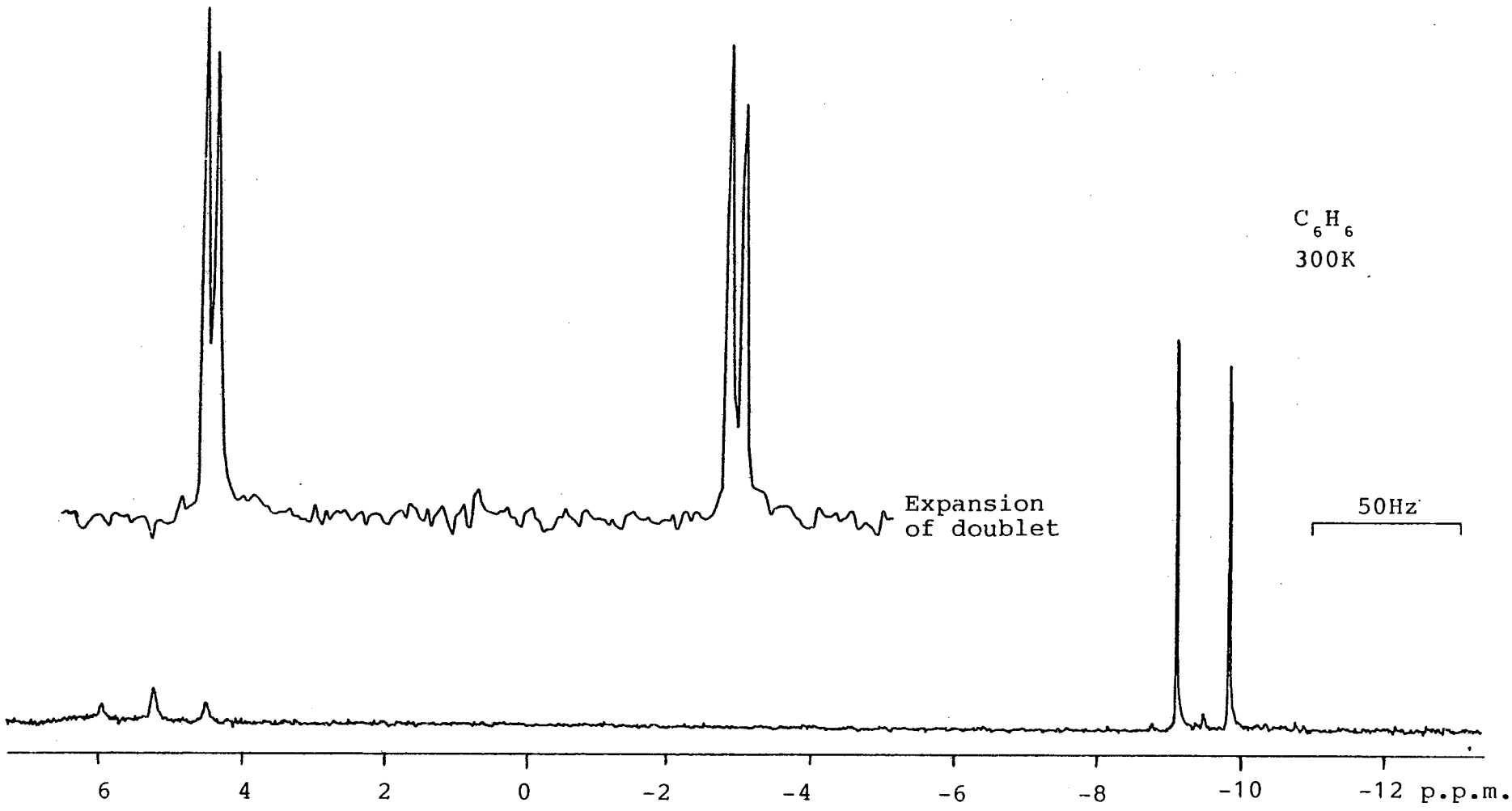
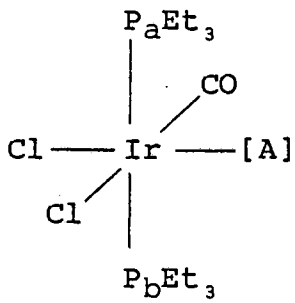


Table 2 N.m.r. parameters for



Parameter \ [A]	P'HClSe	P'HSe(Se'H)	P'H Se
δP' /p.p.m.	-9.1	-60.1	-105
δP_a /p.p.m.	-9.1	-11.1	-14.2
δP_b /p.p.m.	-16.1	-14.1	
δH /p.p.m.	7.4	7.44	4.2
δSe /p.p.m.	245	32.2	-168
δSe' /p.p.m.	-	324	-
^1J(P',H) /Hz	482	437	405
^1J(Se,P') /Hz	687	596	534
^1J(Se',P') /Hz	-	317.1	-
$^2J(P_a,P_b)$ /Hz	318.7	322	-
^2J(P,P') /Hz	13	14	14
$^3J(P_a,H)$ /Hz	9.8	11.6	6.4

All the parameters recorded in toluene; [A] = $P'H_2Se$ at 300K, others at 220K.

4.1(f) Hydrogenselenide

This reaction has been examined before [53], but a number of the ^{77}Se resonances were not observed. These have now been obtained and confirm the structures as $[Ir(CO)Cl_2(PEt_3)_2(P'HClSe)]$, $[Ir(CO)Cl_2(PEt_3)_2(P'H_2Se)]$ and $[Ir(CO)Cl_2(PEt_3)_2\{P'HSe(Se'H)\}]$. Full n.m.r. parameters are given in Table 2 and the reaction scheme is as follows:

$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$

15min. | H_2Se
300K ↓ -HCl

$[Ir(CO)Cl_2(PEt_3)_2(P'ClHSe)]$

2hrs. | H_2Se
↓ -HCl

$[Ir(CO)Cl_2(PEt_3)_2\{P'HSe(Se'H)\}]$

12hrs. | -Se
↓

$[Ir(CO)Cl_2(PEt_3)_2(P'H_2Se)]$

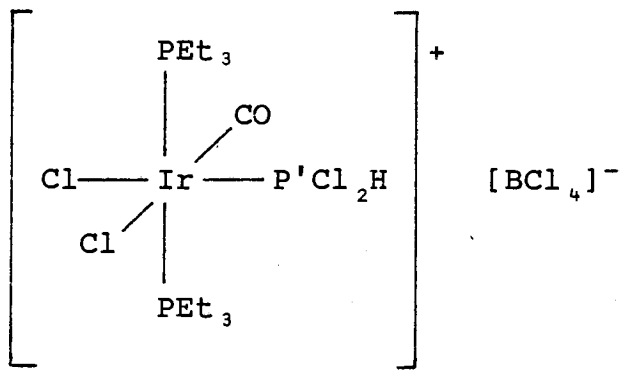
4.1(g) Hydrogenchloride with Borontrichloride

Previous work has shown that hydrogenchloride reacts slowly at low temperatures with $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$, and leads to cleavage of the Ir-P' bond [53]. In this experiment, hydrogenchloride was added at 180K, followed by borontrichloride. The $^{31}P-\{^1H\}$ n.m.r. spectrum at 190K showed a doublet in the $-PEt_3$ region (these peaks were broad and $^2J(P,P')$ was not always resolved) and a broad resonance ($W_{\frac{1}{2}} \simeq 170Hz$) at 42.8 p.p.m. (Figure 34). Some $[Ir(CO)Cl_2H(PEt_3)_2]$ was present also. The shift of the P' resonance to low frequency

(from 304 to 43 p.p.m.) implies an increase in the co-ordination number at P'. When proton coupling was retained, the P' resonance split into a doublet ($^1J(P',H)$ = 580Hz) (Figure 34), showing that one H was bound to P'. These resonances remained broad up to 300K.

The ^1H n.m.r. spectrum showed a wide doublet of broad peaks ($W_{\frac{1}{2}} \simeq 100$Hz) due to the P' proton, and these were unchanged as the sample was warmed to 300 K.

The ^{11}B n.m.r. spectrum at 303K showed a singlet at 8.2 p.p.m. ($W_{\frac{1}{2}} \simeq 9.4$Hz). When the solution was cooled to 180K, the singlet moved to 7.4 p.p.m. and sharpened slightly ($W_{\frac{1}{2}} \simeq 5.1$Hz). This behaviour is similar to that of $[NMe_3H][BCl_4]$ (see Appendix 2), indicating that the ^{11}B resonance is from $[BCl_4]^-$. The structure of the iridium complex is shown below.



$\delta P'$ = 42.8 p.p.m. $^1J(P',H)$ = 569Hz

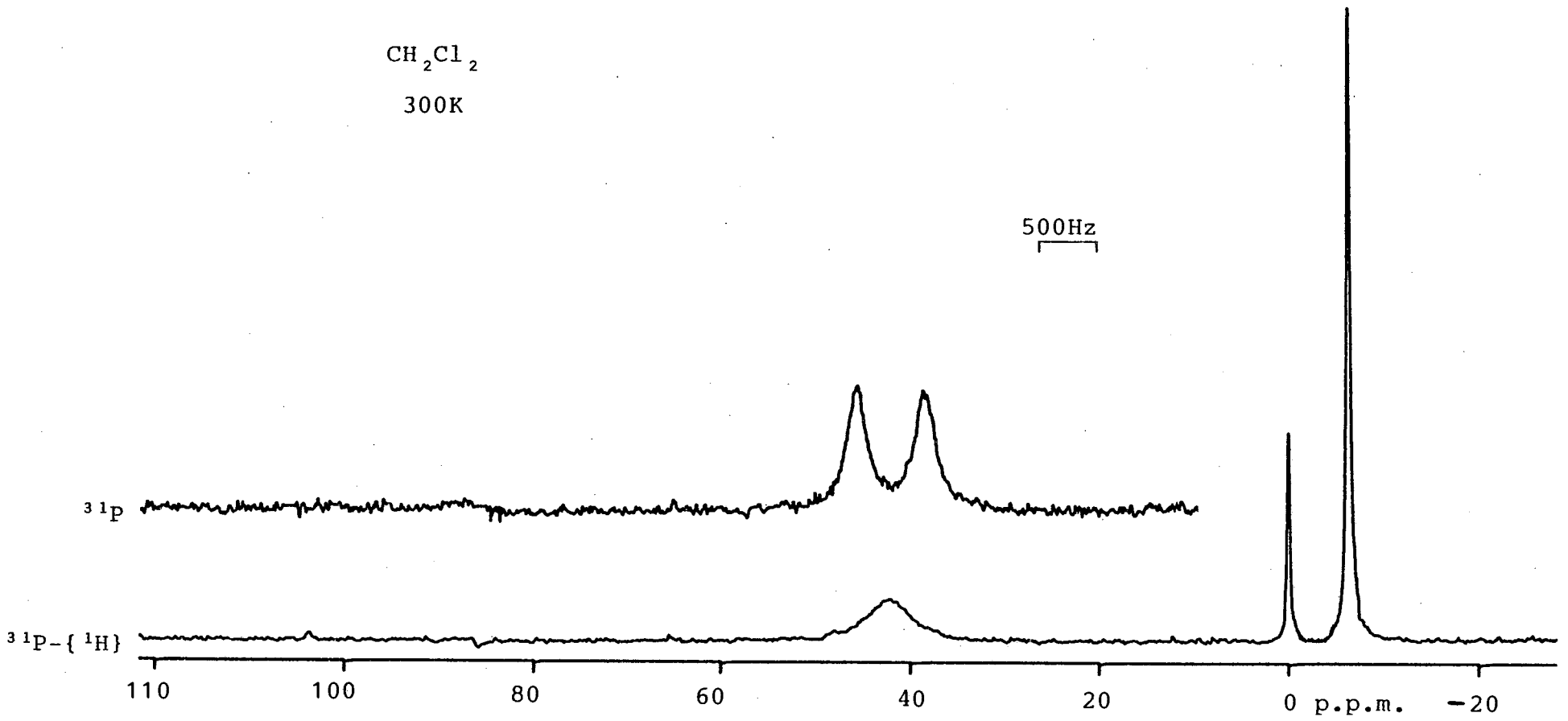
δP = -5.8 p.p.m. $^2J(P,P')$ = ca 10Hz

δH = 8.78 p.p.m. $^3J(P,H)$ not resolved

δB = 7.4 p.p.m. (at 180K)

Parameters were recorded in dichloromethane at 300K.

Figure 34 24.2MHz-^{31}P-$\{^{1}H\}$-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ + HCl + BCl_3



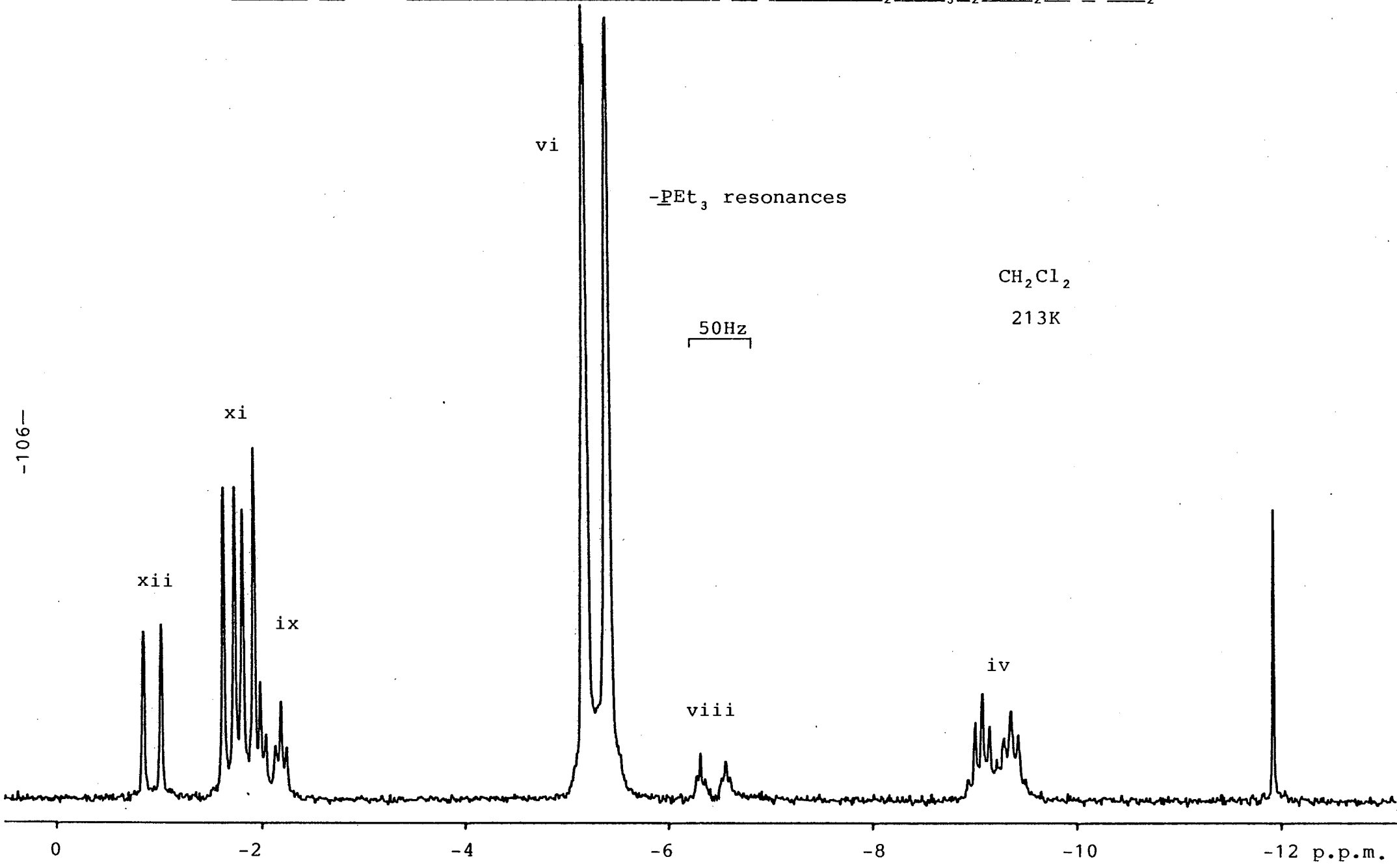
4.1(h) Xenondifluoride

Shortly after allowing reaction to occur at room temperature, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum was examined at 220K and this showed seven species, (Figure 35) all of which were identified from their parameters; trans-$[Ir(CO)Cl_3(PEt_3)_2]$, (iv), (vi), (viii), (ix), (xi) and (xii); these are ionic or molecular forms of $[Ir(CO)Cl_2(PEt_3)_2(PCl_nF_{4-n})]$, and details are given in Sections 3.1(b) and 4.1(j).

In order to determine which of the species (x) and (xi) was the molecular and which the ionic form of $[Ir(CO)Cl_2(PEt_3)_2(PCl_3F)]$, we repeated this reaction but then added an equimolar quantity (with respect to starting material) of borontrichloride. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 220K showed five species which were identified from their parameters; trans-$[Ir(CO)Cl_3(PEt_3)_2]$, (vii), (ix), (xi) and (xii). These observations show that the species (x) seems likely to be $[Ir(CO)Cl_2(PEt_3)_2(PCl_3F)]$ and (xi) may be $[Ir(CO)Cl_2(PEt_3)_2(PCl_2F)][BCl_4]$. Most of the n.m.r. parameters are given in Table 1, but those of (xii) are in Table 3.

The ^{11}B n.m.r. spectrum at 180K showed a broad peak at 8.74 p.p.m. ($W_{\frac{1}{2}} \simeq 230Hz$). The BCl_3 must have removed fluoride ions since (iv) had been converted to (vii). Exchange between the boron halides present may be causing the broad line in the ^{11}B n.m.r. spectrum.

Figure 35 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ + XeF_2



4.1(i) Phosphoruspentachloride

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the solution of a 1:1 molar ratio of the reactants shows no reaction at 180K, but at 280K reaction does occur (Figure 36). Some $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ is still present, along with $[Ir(CO)Cl_2(PEt_3)_2(PCl_3)]^+$ (xii) (see Section 4.1(j)). Singlets which may be assigned to PCl_3 and $[PCl_6]^-$ are also present [167]. The following reaction scheme is consistent with the results:

$$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)] + 2PCl_5 \longrightarrow [Ir(CO)Cl_2(PEt_3)_2(PCl_3)]^+ + [PCl_6]^- + PCl_3$$

4.1 (j) Dichlorine [160]

This reaction has already been discussed [53], but further investigation was necessary to determine the nature of the products. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of a solution in dichloromethane of a 1:1 molar ratio of dichlorine and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ at 300K showed one species (xii) (Figure 37). The spin system is "P_2,P'" with $\delta P' = 64.4$ p.p.m., $\delta P = -2.6$ p.p.m., $^2J(P,P') = 14.0$Hz and we shall later show that $[Ir(CO)Cl_2(PEt_3)_2(PCl_3)]^+$ is the formula of (xii). During reaction, a white solid precipitated from the solution. Further investigation of this solid (v) was then attempted, and it was isolated by pipetting away the solvent, and washing the solid with dichloromethane.

The solid (v) was noted to be only slightly soluble in dichloromethane, acetonitrile or nitromethane and when an attempt at $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy was

Figure 36 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)] + PCl_5$

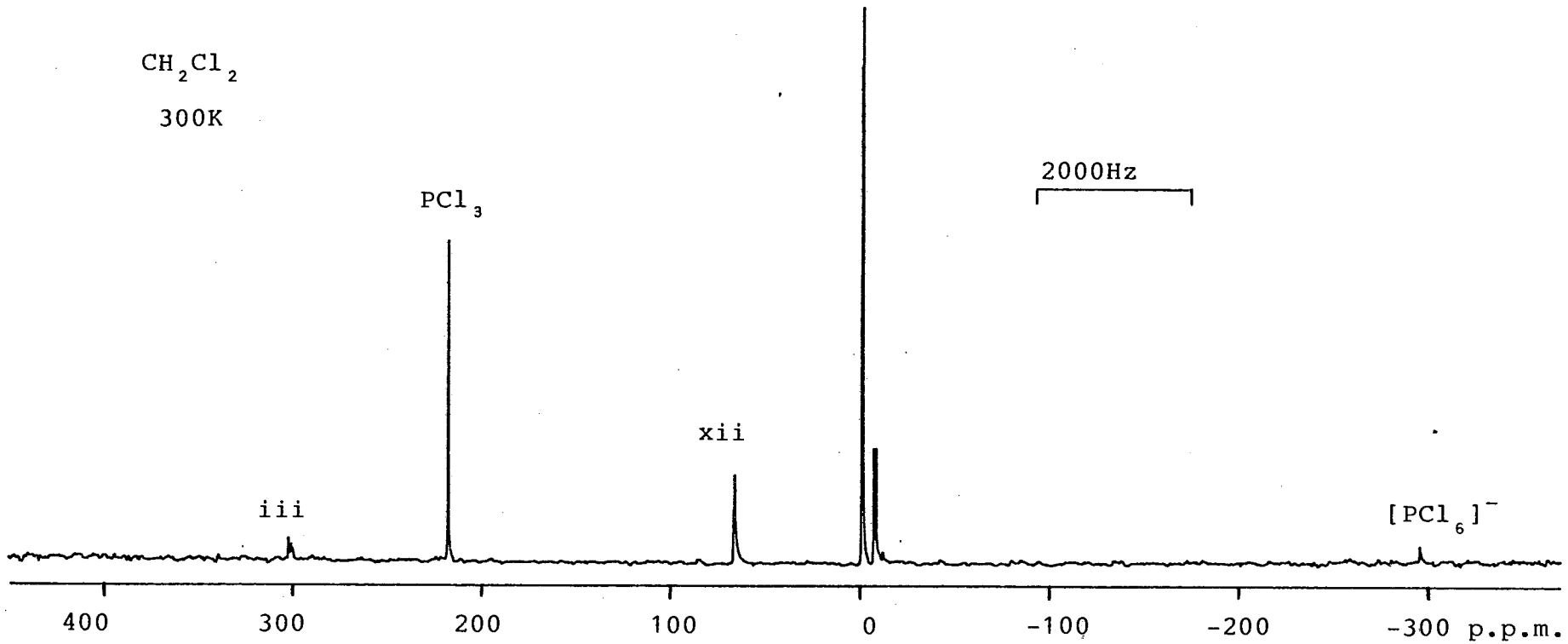
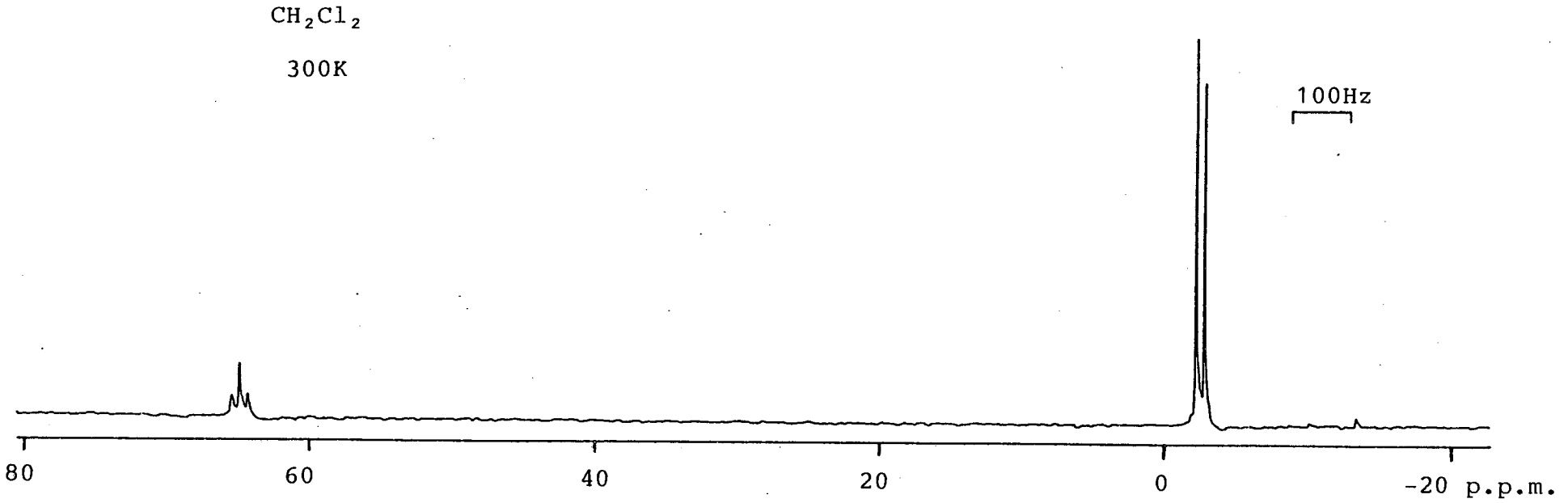


Figure 37 24.2MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)] + Cl_2$



carried out in dichloromethane, solid was present in the n.m.r. tube. After a fairly long accumulation of data, the spectrum obtained showed that there were small amounts of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ (see Section 4.1(d)) and (xii) present. The former compound has now been shown to be the product of hydrolysis of the solid (v), and must have formed during the isolation. The compound (xii) could not have arisen from dissolution of the solid, as there was much less present in this solution than in the original solution of dichlorine and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$. We believe that the washing of the solid (v) was inefficient and some (xii) remained from the original solution. Clearly two products have been formed in this reaction, namely (xii) and a solid (v). This solid seems not to be sufficiently soluble for us to obtain its n.m.r. parameters, but we are able to carry out other tests to attempt to characterise it.

Repeated examination of the infra-red spectrum of (v) shows that an absorption at $2080cm^{-1}$ (assigned to CO stretch) slowly collapses and is replaced by an absorption at $2060cm^{-1}$ (CO stretch in $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$). At the same time an absorption at $1215cm^{-1}$ (PO stretch in $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$) appears and increases in intensity. We believe this change to be caused by the hydrolysis of (v).

Attempts to obtain the mass spectrum gave molecular ion peaks from $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ and $[Ir(CO)Cl_2(PEt_3)_2\{PCl_2(OH)_2\}]$, but we believe that the

compound had hydrolysed before its mass spectrum was measured.

Elemental analysis for C, H and Cl is consistent with a formula that contains two more chlorine atoms than $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$. The reactivity of the solid was then investigated.

4.2 Reactions of the Solid (v)

4.2(a) Borontrichloride

The $^{31}P-\{^1H\}$ spectrum at 303K of a solution of equimolar amounts of solid (v) (assumed to contain one mole more of dichlorine per iridium than $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$) and BCl_3 showed that reaction had occurred to give a single species whose n.m.r. parameters were identical to those of (xii). No solid remained in the n.m.r. tube. At 303K the ^{11}B n.m.r. spectrum showed a sharp singlet at 7.4 p.p.m. which can be assigned [167] to $[BCl_4]^-$ ($W_{\frac{1}{2}} \simeq 0.6$Hz).

This reaction was carried out a number of times, but the ^{11}B n.m.r. spectrum did not always show a sharp peak. We believe that small amounts of borontrichloride can cause a broadening of the $[BCl_4]^-$ resonance and this is discussed in Appendix 2.

4.2(b) Aluminiumtrichloride, Al_2Cl_6

The dichloromethane solution of a mixture of solid (v) and Al_2Cl_6 in a 2:1 molar ratio gave a $^{31}P-\{^1H\}$ n.m.r. spectrum at 300K identical to that of the solution of BCl_3 and the solid. The ^{27}Al n.m.r. spectrum showed a sharp singlet ($W_{\frac{1}{2}} \simeq 10$Hz) at 102.8 p.p.m. which may be

assigned [167] to $[AlCl_4]^-$. It would seem that (xii) was formed here also.

4.2(c) Triethylphosphine

The $^{31}P-\{^1H\}$ n.m.r. spectrum of a solution in dichloromethane of triethylphosphine and the solid (v) showed that the reaction had occurred to give $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and a singlet resonance at 111.9 p.p.m. (Figure 38). The literature value for PEt_3Cl_2 is 112.2 p.p.m. [195], which was confirmed by our own synthesis of this compound, so we may assign the singlet in the spectrum to PEt_3Cl_2. A singlet present at about 20 p.p.m. is believed to be $[Ir(CO)Cl(PEt_3)_2]$.

4.2(d) $[Ir(CO)Cl(PEt_3)_2]$

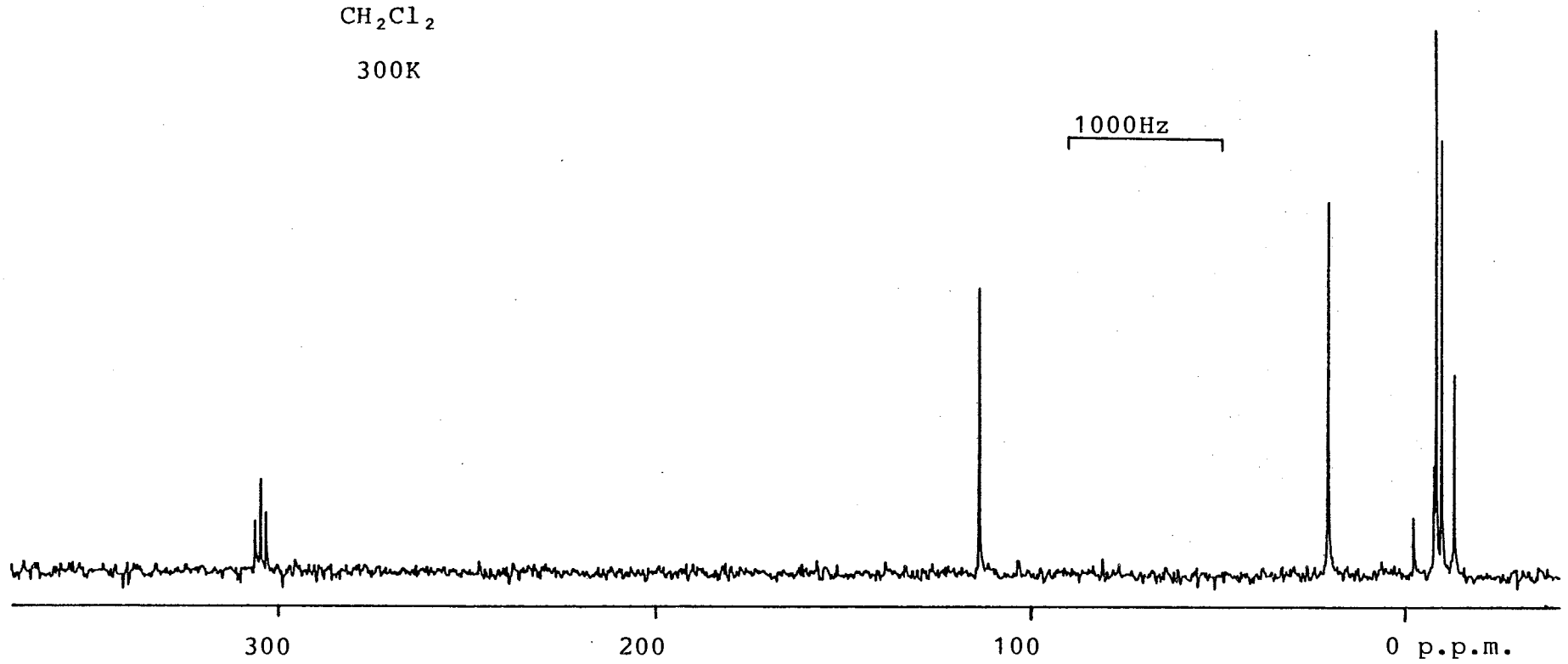
The reaction at room temperature between the solid (v) and $[Ir(CO)Cl(PEt_3)_2]$ was examined in dichloromethane solution by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The two species present were identified as $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and trans-$[Ir(CO)Cl_3(PEt_3)_2]$.

The last two reactions confirm the formulation of the solid as containing one mole of dichlorine more than $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$. The formula $[Ir(CO)Cl_2(PEt_3)_2(PCl_3)]^+$ for (xii) is consistent with these results.

4.2(e) Water

The $^{31}P-\{^1H\}$ n.m.r. spectrum of a solution in CH_2Cl_2 of the solid (v) and a tenfold molar excess of water at room temperature showed resonances identical to those of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$. When the solid is

Figure 38 24.2MHz-^{31}P-{^{1}H}-spectrum of Compound (v) + PEt_3



treated with excess trimethylamine and water under the same conditions, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum shows only a singlet resonance from $[Ir(CO)Cl(PEt_3)_2]$. The reaction in the absence of solvent was examined by infra-red spectroscopy, which showed that hydrogenchloride gas was released. The infra-red spectrum of the solid was described in Section 4.1(j).

4.3 Reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$

A limited study of the reactivity of this compound was carried out: there was no reaction between $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ and $[Ir(CO)Cl(PEt_3)_2]$ or triethylphosphine, but reaction did occur with BCl_3 and Al_2Cl_6.

4.3(a) Borontrichloride

An equimolar mixture of the reactants gave a $^{31}P-\{^{1}H\}$ n.m.r. spectrum which showed that the resonance had shifted to higher frequency, and was much broader ($W_{\frac{1}{2}} \simeq 50Hz$) (Figure 39). The ^{11}B n.m.r. spectrum showed a doublet ($W_{\frac{1}{2}} \simeq 15Hz$) indicating that the boron is coupling to P'. The structure shown below is consistent with these results.

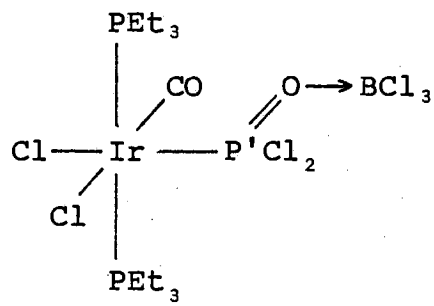


Figure 39 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ + BCl_3

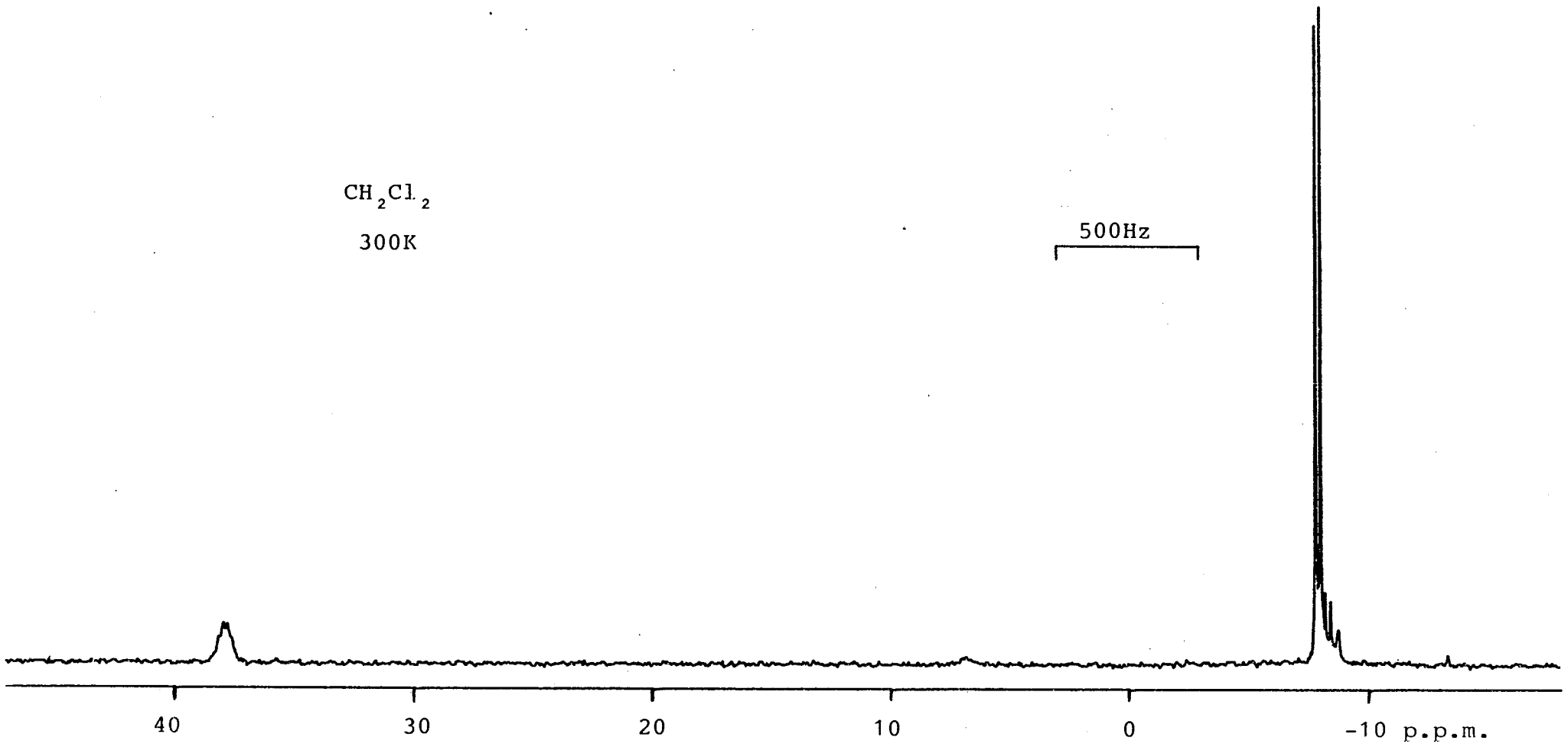
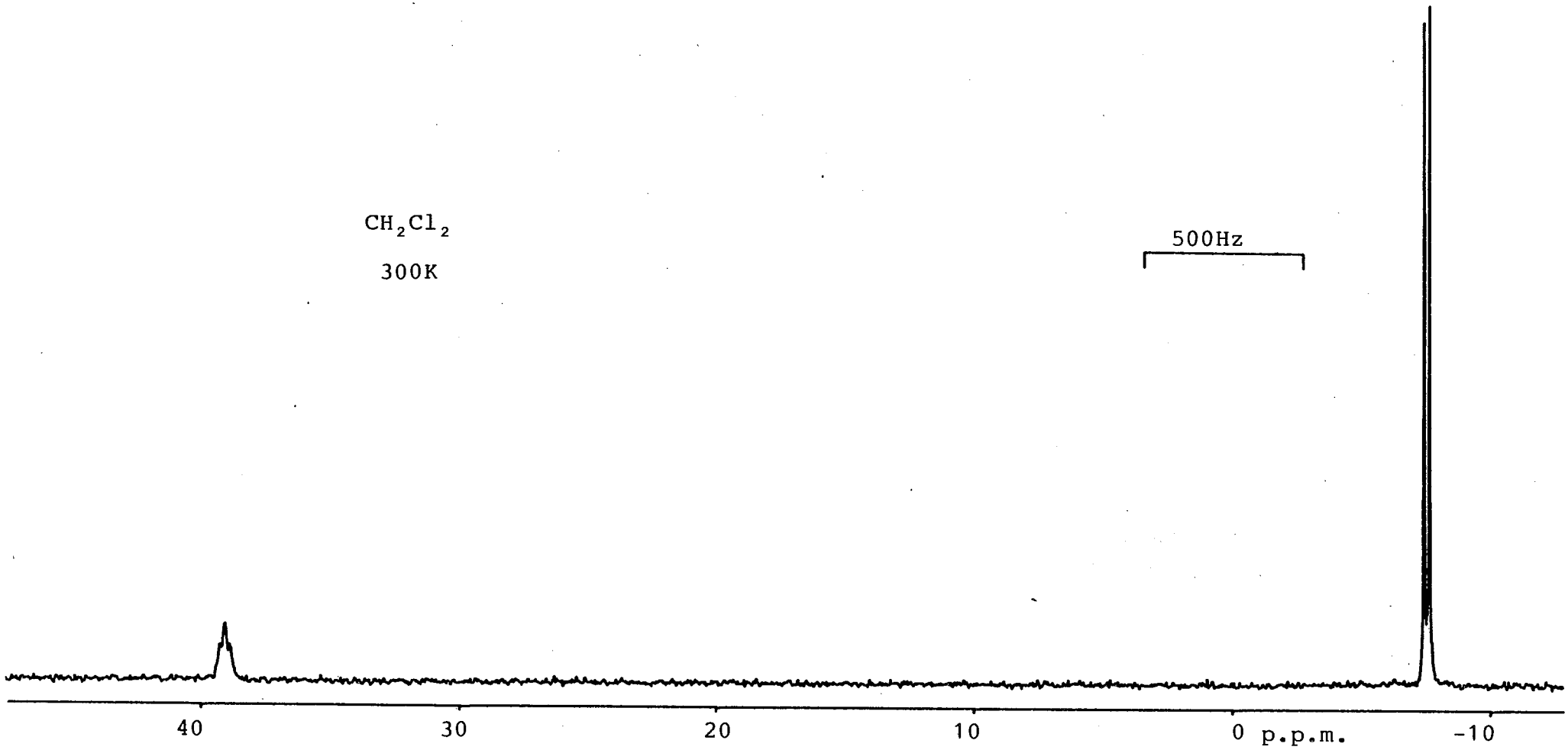


Figure 40 81.0MHz-^{31}P-{^{1}H}-spectrum of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)] + \frac{1}{2}Al_2Cl_6$



$\delta P'$= 38.2 p.p.m. $^2J(P,P')$ = 16.5Hz

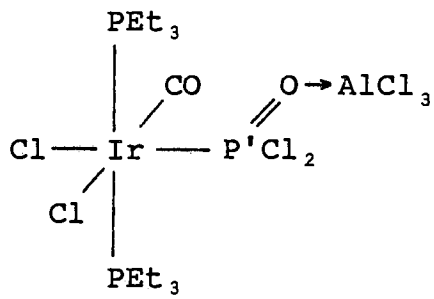
δP = -7.7 p.p.m. $^2J(P',B)$ = 10.5Hz

δB = 7.6 p.p.m.

All parameters were recorded in dichloromethane at 300K.

4.3(b) Aluminiumtrichloride

The $^{31}P-\{^1H\}$ n.m.r. spectrum of this reaction is shown (Figure 40). The P' resonance has shifted to higher frequency by about 30 p.p.m. ($W_{\frac{1}{2}} \simeq 40Hz$). The structure shown below is tentatively suggested as the product.



$\delta P'$= 39.9 p.p.m. $^2J(P,P')$ = 16.6Hz

δP = -7.2 p.p.m.

All parameters were recorded in dichloromethane at 300K.

4.4 Discussion

In attempting to form "bridges" with the $-PCl_2$ group of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ the compounds $[Pt(cod)Cl_2]$ and $[\{RuCl_2(p\text{-cymene})\}_2]$ have been shown not to react. This is in contrast to the $-PF_2$ bridged species formed by reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ with such substrates [53]. This lack of reactivity may be because of steric factors; the larger chlorine atoms preventing reaction. Indeed the $-PCl_2$ group is able to bridge to the

smaller groups such as BCl_3 and BH_3. The lack of reactivity with respect to BF_3 may be because of electron donation from the filled fluorine p orbitals into the empty p orbital on boron, which makes BF_3 a weaker Lewis acid than BCl_3. However, the relative ease of protonation of the $-PF_2$ group compared with the $-PCl_2$ group leads to more firm conclusions. Since neither of the protonated species precipitates, it would seem that the $-PF_2$ group is more basic than the $-PCl_2$ group. The reluctance of $-PCl_2$ groups to form "bridges" is consistent with its apparently less basic character.

In many of the reactions examined in this work cationic metal complexes are frequently observed. These seem to be produced when there is the possibility of formation of a stable anion, for example in the reaction of $[Ir(CO)Cl(PEt_3)_2]$ with PF_3Cl_2 and PF_4H the anions Cl^- and $[PF_5H]^-$ respectively are formed. The reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ with PF_5 and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with PCl_5 lead to the formation of $[PF_6]^-$ and $[PCl_6]^-$. In a similar way we have noted the formation of cationic metal complexes where dichlorine may have reacted to give the Cl_3^- ion.

The reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with xenondifluoride and dichlorine also require some discussion. Reaction of dichlorine with either species leads to ionic compounds since in both cases there is the chance of chloride loss. In the reactions with xenondifluoride there is no

possibility of loss of chloride with $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$, and even reaction with $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ gives products which are mostly molecular.

The structure of the solid (v), formed exclusively in the reaction of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with dichlorine, remains problematic. There is no doubt that (v) contains two more chlorine atoms per iridium than $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$. One possible structure for (v) is $[Ir(CO)Cl_2(PEt_3)_2(PCl_4)]$, but this structure would not account for the low solubility of (v) since all our other products are soluble.

An alternative is the ionic structure $[Ir(CO)Cl_2(PEt_3)_2(PCl_3)][Ir(CO)Cl_2(PEt_3)_2(PCl_5)]$. This may explain the low solubility in dichloromethane, but we might expect it to be more soluble in nitromethane. There is clearly a need for further work on this reaction. Mass spectroscopy may give useful data, especially if FAB techniques are employed as cations and anions can be observed separately [199]. The low solubility of the solid may however give rise to problems in obtaining a FAB spectrum.

Table 3 N.m.r. Parameters for $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ and some Derivatives

Compound		δP'	δP	δB	$^1J(P',B)$	$^2J(P,P')$	T/K	Other
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$a	(iii)	304.0	-9.2	-	-	34.0	300	$\delta^{13}C$ = 162.7 p.p.m.
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2H)][BCl_4]$b		42.8	-5.8	7.4	-	ca10	300	$\delta P'\underline{H}$ = 8.78 p.p.m. $^1J(\underline{P}',H)$ = 569Hz $^3J(P,H)$ n.r.
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_3)][BCl_4]$b	(xii)	64.6	-0.9	7.4	-	14.0	220	-
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2O)]$b		6.45	-8.1	-	-	17.1	300	-
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2S)]$c		44.2	-10.7	-	-	13.7	300	-
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2Se)]$c		19.2	-11.6	-	-	12.4	300	$\delta^{77}Se$ = 581.3 p.p.m. $^1J(Se,P')$ = 775Hz
$[Ir(CO)Cl_2(PEt_3)_2\{P'(BCl_3)Cl_2\}]$b		127.8	-6.6	7.0	137	6.1	190	-
$[Ir(CO)Cl_2(PEt_3)_2\{P'(BH_3)Cl_2\}]$b		190.1	-9.0	-19.1	n.r.	4.55	270	$\delta B\underline{H}$ = 2.0 p.p.m. $^1J(B,H)$ = 100Hz

Chemical shifts are given in p.p.m. and coupling constants in Hz.
a in toluene, b in dichloromethane, c in chloroform, n.r. means not resolved.

Chapter 5

Experimental

5.1 Vacuum Line Techniques

All volatile compounds were handled on a pyrex vacuum line of conventional design [200]. The line was built from detachable sections; Apiezon N and L greases were used on taps and joints respectively. Detachable reaction ampoules were fitted with Rotaflo or Sovirel greaseless taps. Schlenk tubes were attached to the line via cone-to-cone tap adaptors. The vacuum was maintained by a mercury diffusion pump assisted by a rotary oil pump.

Pressure of non-condensable gas in the line was checked by a Pirani ~~guage~~ gauge. The pressure of materials inside sections of the line were measured using a spiral guage with mirror, used as a null point instrument with a lamp and scale. The line was calibrated for volume using a molecular weight bulb. Accurate volumes for individual sections combined with pressure readings allowed accurate measurement of volatile materials.

5.2 Handling of Air-sensitive Solids

Air-sensitive solids were prepared and handled on a Schlenk vacuum-and-nitrogen line using high purity dinitrogen (BOC white spot, specified less than 0.5% H_2O and O_2). Preparations were carried out in pyrex reaction vessels with tapped side arms to allow evacuation, evaporation of solvents and addition of dinitrogen. Reactions were agitated with teflon coated stirrer bars.

5.3 Reactions in Sealed N.M.R. Tubes

Reactions of this type were used extensively throughout this thesis in order to observe reactions as

they took place. In a typical reaction 0.1 mmole of metal complex was weighed into an n.m.r. tube with a B10 cone extension. The tube was evacuated and deuterated solvent was distilled in to a depth of 3cm. The complex was then dissolved. The required amount of volatile reactant was condensed into the tube, which was sealed and stored at liquid nitrogen temperature. Spectra were then recorded at the desired temperature.

For reactions involving solids or liquids the dissolved complex was kept at liquid nitrogen temperature while the n.m.r. tube was filled with dry nitrogen using a tapped adaptor. The reactant was added to the frozen tube, which was then evacuated, sealed and handled in the normal manner.

5.4 Isolation of Complexes

Complexes were often isolated in the following way. The sealed n.m.r. tube in which the reaction had been observed was opened under nitrogen and the contents poured into a Schlenk tube. The n.m.r. tube was washed with dichloromethane. The solution was then "layered" with n-pentane, and the Schlenk tube stoppered and sealed with sealing tissue, to avoid using grease. After the solid had precipitated, the solvent was pipetted away and the solid dried under vacuum. Where crystalline materials were produced, they were examined with a view to performing an X-ray crystal structure analysis.

5.5 Instruments and Elemental Analysis

The n.m.r. spectra were recorded on the following instruments, all of which use a deuterium field / frequency lock: Brucker WH360 (^{1}H, ^{11}B, ^{13}C, ^{27}Al, ^{31}P, ^{77}Se and ^{119}Sn), Brucker WP200 (^{1}H, ^{11}B, ^{31}P and ^{77}Se), Brucker WP80 (^{1}H and ^{19}F), Varian XL100 (^{19}F and ^{31}P) and Jeol FX60Q (^{31}P). Chemical shifts were measured in p.p.m. as positive to high frequency of the following references: 85% H_3PO_4 (for P), $BF_3(OEt_2)$ (for B), Me_2Se (for Se), $[Al(OH_2)_6]^{3+}$ (for Al), CCl_3F (for F), $SnMe_4$ (for Sn) and $SiMe_4$ (for C,H).

Infra-red spectra were recorded using Perkin Elmer 577 and 598 double beam spectrometers (250 to 4000 cm^{-1}). Spectra of solids were obtained as nujol or hexachlorobutadiene mulls between CsI disks; gas phase spectra were recorded using a gas cell fitted with KBr disks.

Mass spectra were obtained on a Kratos-80RF spectrometer operating in the FAB mode [199]. The compounds were dissolved in diamylphenol before being inserted into the spectrometer.

Analyses for carbon, hydrogen and nitrogen were carried out using a Perkin Elmer 240 elemental analyser. Analysis for chlorine was carried out using the oxygen flask combustion technique; a mixture of 6% hydrogenperoxide and 1ml. 0.5M potassium hydroxide was used as absorbent. After boiling, ethanol was added and the pH adjusted to neutrality using 0.5M nitric acid and

0.05M potassium hydroxide. The pH was then lowered to the correct value for the titration which used bromophenolblue (yellow at this pH) and diphenylcarbazone as indicator. This mixture was titrated against 0.01M mercuric nitrate giving a deep purple colour when excess Hg^{2+} is present at the end point.

5.6 Experimental for Chapter 2

5.6(a) Synthesis of $[Ir(CO)Cl(PEt_3)_2]$ [201]

The complex $[\{Ir(C_8H_{14})_2Cl\}_2]$ (C_8H_{14} = cyclooctene) was prepared from $[IrCl_3(OH_2)_5]$ by literature methods [202]. Next, 0.45g. of $[\{Ir(C_8H_{14})_2Cl\}_2]$ was stirred for 15 minutes under nitrogen in 5ml. of dry degassed acetone. At room temperature, carbonmonoxide (BOC technical grade) was slowly bubbled through the slurry for 4 to 5 minutes, during which time it turned dark blue. A solution of 0.3ml of triethylphosphine in 5ml acetone was then added to the blue solution, and the mixture stirred for at least one hour, while it turned a straw yellow colour. Any solids were removed by Schlenk filtration. The solvent was then evaporated and the product heated at 353K for 90 minutes under vacuum. The product was sublimed at 393K under vacuum to yield yellow crystals which were air sensitive, but could be handled for short periods in air.

5.6(b) Other materials

The compounds PCl_2F_3 [203,204], $PClF_4$ [205], HPF_4 [206], PMe_2H [207] and SPhCl [208] were prepared according to the literature. The sample of PMe_2H was kindly supplied by Mr. S.D. Henderson. Most other chemicals were obtained from various chemical companies. The BCl_3 was purified by passing through a 195K bath and using what was retained. The $SiCl_4$ was distilled under nitrogen, and the PCl_3 was kept over molecular sieve A3 to remove HCl. The PMe_2ClO was obtained by air oxidation of PMe_2Cl. Small amounts of Pr^n_4NCl were dried under vacuum before use. The Cl_2 and S_2Cl_2 impurities in the SCl_2 were removed by passage through baths held at 223K and 195K. Water and HCl were removed from Cl_2 by passage through 195K and 153K baths. Solvents were dried over molecular sieve A3. Dichloromethane was stored over potassium hydroxide and then distilled from over calcium hydride. It was stored in an ampoule over calcium hydride until required.

5.6(c) Reactions of $[Ir(CO)Cl(PEt_3)_2]$

All the reactions of $[Ir(CO)Cl(PEt_3)_2]$ were carried out as detailed in section 5.3 using dichloromethane as solvent.

5.6(d) Isolation of Products

This was carried out using the methods in section 5.4. Analysis figures and infra-red spectral data (Table 4) are given.

Table 4

Analysis figures for the Compounds Isolated from Reactions in Chapter 2

Required values are in parentheses.

Compound	%C	%H
$[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$	22.27 (22.09)	4.28 (4.28)
$[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$	20.73 (20.74)	4.0 (4.01)
$[Ir(AsCl_2)(CO)Cl_2(PEt_3)_2]$	22.96 (23.18)	4.24 (4.49)
$[Ir(CO)Cl_2(PEt_3)_2(SCl)]$	26.52 (26.24)	5.22 (5.08)

Infra-red spectra for the Compounds Isolated from Reactions in Chapter 2 (values in cm^{-1})

$[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$

2040vs, 1400s, 1258m, 1032vs, 775vs, 735vs, 565s, 522m, 459m, 364vs, 377vs, 280m, 230w.

$[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$

2040vs, 1400w, 1260w, 1032s, 768s, 740s, 565s, 520m, 455m, 419w, 388w, 327s, 335s, 340s, 352s, 315s, 290m, 280w.

$[Ir(AsCl_2)(CO)Cl_2(PEt_3)_2]$

2018vs, 1418vw, 1260w, 1030s, 765m, 755m, 618w, 570s, 552s, 520m, 420w, 355s, 329s, 301w, 268w.

fac-$[Ir(CO)Cl_3(PEt_3)_2]$

2055vs, 1410w, 1260w, 1250w, 1040s, 772m, 750m, 625m, 570s, 518m, 438m, 392m, 331m, 290s.

trans-$[Ir(CO)Cl_3(PEt_3)_2]$

2040vs, 1415w, 1270w, 1040s, 765m, 741m, 632w, 570m, 530m, 418w, 392w, 334w.

5.7 Experimental for Chapter 3

5.7(a) Synthesis of Iridium Starting Materials

The synthesis of the complex $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ was described elsewhere [53,54] and $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ as described in sections 5.3 and 5.4.

5.7(b) Other materials

The compounds PF_2Cl [209] and HCl [210] were synthesised by literature methods. The XeF_2 was synthesised and kindly supplied by Dr. J.H. Holloway [211]. Anhydrous trimethylamine was obtained from Mr. S.D. Henderson. The compounds Cl_2 and BCl_3 were obtained as described in section 5.6(b). The PF_5 was obtained by thermal decomposition of benzenediazoniumhexafluorophosphate, and purified by literature methods [212].

5.7(c) Reactions of the Iridium Complexes

All the reactions of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ were carried out as detailed in section 5.3 using dichloromethane as solvent.

5.7(d) Isolation of $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

This was carried out using the methods in section 5.4. Analysis figures and infra-red spectral data (Table 5) are given.

Table 5

Analysis figures for $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

Required values are in parentheses.

%C	25.41	(24.61)
%H	5.05	(4.77)
%Cl	12.66	(11.18)

Infra-red spectra for $[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$ and $[Ir(CO)Cl_2(PEt_3)_2(PF_2O)]$ (values in cm^{-1})

$[Ir(CO)Cl_2(PEt_3)_2(PF_4)]$

2030s, 1415w, 1260w, 1210w, 1030s, 899s, 890s, 835s, 730m, 630w, 570m, 550m, 540m, 520w, 500m, 455w, 390vw, 328w, 285w.

$[Ir(CO)Cl_2(PEt_3)_2(PF_2O)]$

2038s, 1415w, 1270w, 1255m, 1200w, 1040s, 830s, 819s, 750m, 570m, 550m, 525w, 422w, 332vw, 295vw, 285vw.

5.8 Experimental for Chapter 4

5.8(a) Synthesis of Iridium Starting Materials

The complex $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ was synthesised as described elsewhere [53,56]. The complex $[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$ was synthesized as described in sections 5.3 and 5.4.

5.8(b) Other materials

The compounds Cl_2, BCl_3, PCl_5 and others were obtained as described in section 5.6(b); HCl and XeF_2 as in section 5.7(b). The compounds B_2H_6 [213], Se_8 [210], H_2Se [210], $[Pt(cod)Cl_2]$ [214] and $[\{RuCl_2(p\text{-cymene})\}_2]$ [215] were synthesized by literature methods. The metal complexes were kindly supplied by Dr. T.A. Stephenson; $[PtCl_2H_2(PEt_3)_2]$ which was obtained by reaction of $[PtClH(PEt_3)_2]$ with HCl was kindly supplied by Mr. S.D. Henderson. The Al_2Cl_6 was purified by sublimation under vacuum at 373K. The N_2O_4 was obtained by heating $Pb(NO_3)_2$ to decomposition and fractionating through a 195K bath. The BF_3 was obtained as follows: a sample of $BF_3(OEt_2)$ was fractionated using a 128K bath. Small amounts of BF_3 and HCl passed through this trap and were collected at 177K. This mixture was subsequently surrounded by a 128K bath whilst still frozen, any substances boiling off being collected in a 177K bath. These were found to consist mainly of HCl. By repeating this latter process, fairly clean BF_3 was produced in very small amounts.

5.8(c) Reactions of the Iridium Complexes

The reactions of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with Se_8 and H_2Se are described elsewhere [53,56]. The reaction of $[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ with dichlorine was carried out as described elsewhere [53], but dichloromethane was used as solvent. All the other reactions were carried out as detailed in section 5.3, using dichloromethane as solvent.

5.8(d) Isolation of Complexes

Isolation of the products was as described in sections 5.4 and 4.1(j). Analysis figures, infra-red data and mass spectroscopic data are given in Table 6.

Table 6

Analysis figures for the Compounds Isolated from Reactions in Chapter 4 Required values are in parentheses.

$[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$		Solid (v)	
%C	24.44 (24.20)	%C	22.19 (22.30)
%H	4.89 (4.69)	%H	4.31 (4.32)
%Cl	22.25 (21.98)	%Cl	31.3 (30.38)

Infra-red spectra for the Compounds Isolated from Reactions in Chapter 4 (values in cm^{-1})

$[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$

2065vs, 1260m, 1215s, 1040s, 775m, 750m, 720m, 565s, 530m, 525s, 505s, 500s, 475s, 420w, 390w, 330w, 295w, 285vw.

Compound (v)

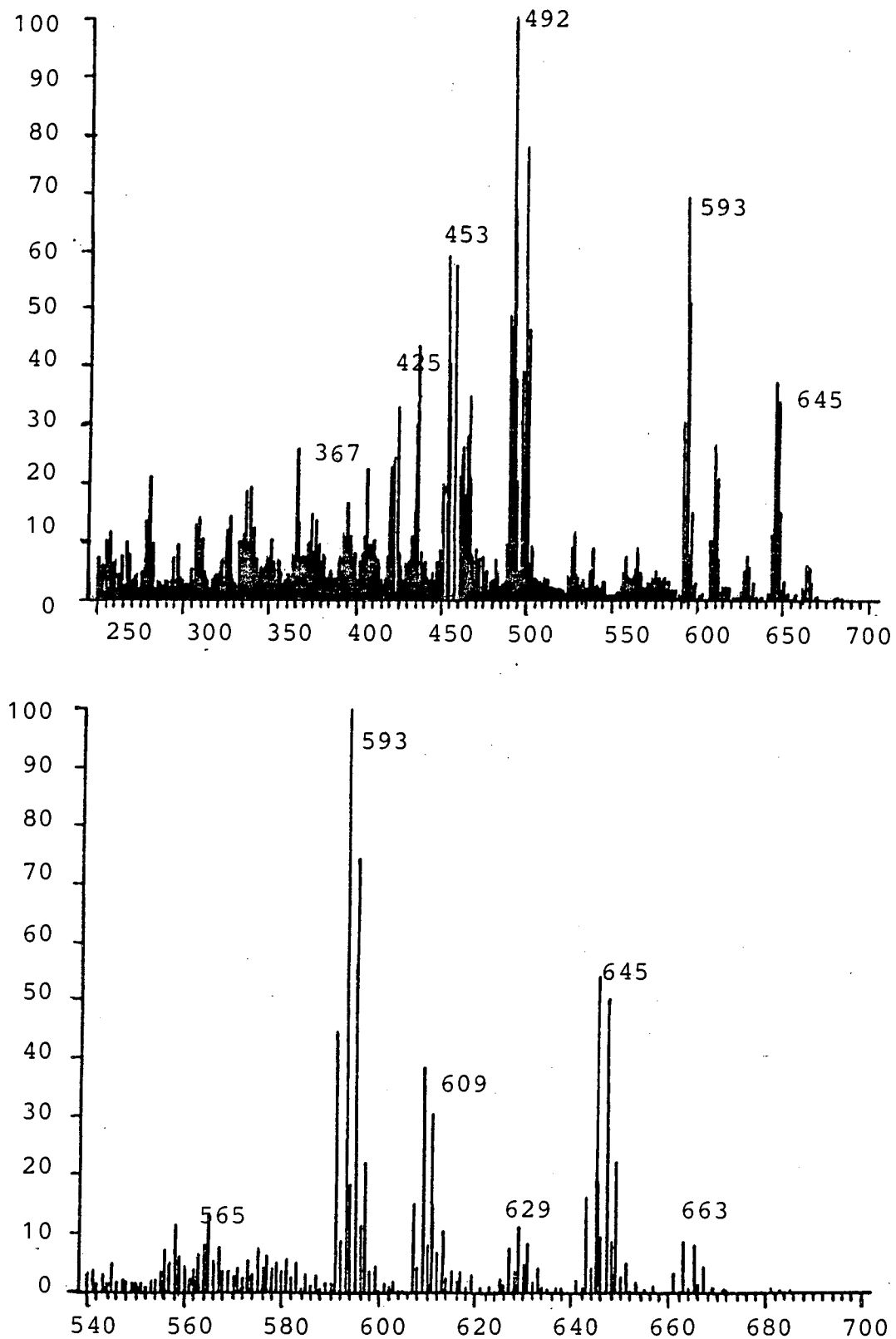
2080vs, 1260m, 1040s, 775m, 720m, 575s, 552s, 539m, 500m, 475m, 422w, 385w, 340w, 318w.

Mass Spectroscopic Data for Compound (v) (see Figure 41)

$[Ir(CO)Cl_2(PEt_3)_2\{PCl_2(OH)_2\}]$	m/z 663 ($[M+1]^+$, 5%)
$[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$	m/z 645 ($[M+1]^+$,40%)
$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$	m/z 629 ($[M+1]^+$,10%)
$[Ir(CO)Cl_2(PEt_3)_2\{PO(OH)_2\}]$	m/z 609 ($[M+1]^+$,25%)

Figure 41

Mass Spectrum (FAB) of Compound (v)



Appendix 1

X-ray Crystal Structures

In this appendix we shall briefly discuss the molecular structures obtained from X-ray diffraction studies on the complexes isolated in this thesis.

All the structures show an approximately regular octahedral co-ordination geometry at iridium. It is important to compare the different Ir-Cl distances so as to place the ligands in order of trans influence [216] and these are given in Table 7. The mean Ir-CO distance in these molecules is 2.354(20)Å, so the groups $-GeCl_3$, $-SnCl_3$, $-PCl_2$, $-PCl_2O$ and $-PEt_3$ have approximately the same trans influence, all having a higher trans influence than -CO and -Cl groups.

Table 7

Ir-Cl (trans to L) Distances in some Iridium(III) Complexes

Complex	L	Å
$[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$	$-GeCl_3$	2.431(11)
$[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$	$-SnCl_3$	2.424(12)
$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$	$-PCl_2$	2.431(6)
$[Ir(CO)Cl_2(PEt_3)_2(PCl_2O)]$	$-PCl_2O$	2.412(6)
trans-$[Ir(CO)Cl_3(PEt_3)_2]$	-Cl	2.366(3)
fac-$[Ir(CO)Cl_3(PEt_3)_2]$	$-PEt_3$	2.4210(15)
fac-$[Ir(CO)\{Cl_3(AsCl_3)\}(PEt_3)_2]$	$-PEt_3$	2.430(10)
fac-$[Ir(CO)\{Cl_3(AsCl_3)\}(PEt_3)_2]$	$-PEt_3$	2.450(9)

Most of the structures have similar co-ordination at iridium, with one ligand different for each structure. For the structures $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (A) and

$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2O)]$ (B), the P'-Cl bond is shorter in (B) than in (A). This difference is reflected in the shortening from gaseous PCl_3 (d(PCl) = 2.039Å) [217] to PCl_3O (d(PCl) = 1.993Å) [218]. The Cl-P'-Cl angles in (A) and (B) are smaller than those in PCl_3 or PCl_3O and much smaller than the F-P'-F angles in complexes of the type $[Ir(CO)Cl_2(PEt_3)_2\{P'F_2(Q)\}]$ where Q is O or a transition-metal group [54]. The P'-O bond in (B) (1.50Å) is significantly longer than in PCl_3O (1.45Å) [198], but much shorter than a typical P-O single bond (1.60Å). This suggests that the oxygen carries a significant negative charge. Comparing this with $[Ir(CO)Cl_2(PEt_3)_2(PF_2O)]$, the P-O bond length in the latter (1.446Å) is much closer to that in PF_3O of 1.436Å.

Table 8 Some bond lengths (Å) and angles (°) for (A) and (B)

	(A)	(B)
P'-Cl	2.089(10)	2.051(8)
	2.134(9)	2.061(8)
P'-O	-	1.503(14)
Cl-P'-Cl	97.9(4)	98.5(3)

We may also make a comparison between the variable ligand in $[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$ and $[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$ and the structures of $GeCl_4$ and $SnCl_4$ [219].

Compound	Mean E-Cl Bond length (Å)
$GeCl_4$	2.112(1)
$[Ir(CO)Cl_2(GeCl_3)(PEt_3)_2]$	2.172(17)
$SnCl_4$	2.281(4)
$[Ir(CO)Cl_2(PEt_3)_2(SnCl_3)]$	2.333(23)

Both the tin and germanium structures show a lengthening of the element-chlorine bond upon oxidative addition. This may be because of a loss of electron density from the ligand to iridium, since iridium is more electropositive than chlorine. There are no significant differences between the bond angles at the element for the two structures, but in both cases the chlorines on the ligand are bent away from the plane containing the phosphines and the carbonyl compared with the tetrahedral angle of 109.5°:

	Average angle (°)
Ir-Ge-Cl	118.0(5)
Ir-Sn-Cl	117.9(6)
Cl-Ge-Cl	99.7(6)
Cl-Sn-Cl	99.8(8)

Appendix 2

A Boron N.M.R. Study

In our study of iridium complexes we frequently used borontrichloride in order to discover whether the complex was cationic with chloride as counterion. We therefore examined some reactions of borontrichloride in order to obtain some characteristic ^{11}B n.m.r. spectra. The results are given below:

	T/K	δB/p.p.m.	$W_{\frac{1}{2}}$/Hz
BCl_3	303	47.25	25.8
	193	47.09	57
$[Pr^n{}_4N][BCl_4]$	303	7.63	0.6
	193	7.40	1.2
$BCl_3(NMe_3)$	303	10.55	15.6
	193	10.28	14.5
$HCl + BCl_3$	303	47.28	14
	193	47.09	51
$BCl_3 + [BCl_4]^-$	303	27.4	ca50
		11.90	20
	193	11.20†	125
$[HCl + BCl_3] + NMe_3$	303	10.54§	18
		7.62	6.2
	193	10.29	15
		7.40	3.3

†Only one resonance was observed.

§The relative amounts were as follows. At 303K the resonances at 10.5 and 7.6 p.p.m. were in the ratio 3:4. At 193K the resonances at 10.3 and 7.4 p.p.m. were in the ratio 6:1.

All the parameters were measured in dichloromethane

solutions of approximately 4 mol l^{-1} concentration using a Brucker WP200 spectrometer. Some of the spectra were obtained more than once and there could be up to 20% variation in the linewidth.

The ^{11}B nucleus has a spin of $\frac{3}{2}$ and, as with nuclei which have a spin of $\frac{1}{2}$, the external magnetic field determines the Zeeman states, so we are able to observe nuclear magnetic resonance. However, nuclei with a spin greater than $\frac{1}{2}$ have an electric quadrupole moment, which interacts with an electric field gradient. The electric field in a molecule is caused by the electrons and nuclei, and unless the nucleus is in a position of high symmetry (such as boron in the tetrahedral ion $[BCl_4]^-$) there is a finite electric field gradient.

This quadrupolar interaction causes relaxation of the Zeeman states, so that the lines are broader than for spin $\frac{1}{2}$ nuclei. The breadth reflects the value of the electric field gradient [176]. Faster relaxation, which leads to greater linewidth, is also caused by lowering the temperature [220].

Clearly the results for BCl_3 and $[BCl_4]^-$ fit this pattern. Considering the HCl / BCl_3 mixture it would seem that there was a slight change in the spectra, the $W_{\frac{1}{2}}$ value halved at 303K when HCl was added, so there is some interaction between HCl and BCl_3 as far as ^{11}B n.m.r. spectra are concerned. The presence of a 20% excess of BCl_3 to Q^+ $[BCl_4]^-$ causes broadening of the $[BCl_4]^-$ resonance, possibly because of an exchange process at

boron. The reaction of NMe_3 with HCl / BCl_3 produces some $BCl_3(NMe_3)$ and $[NMe_3H][BCl_4]$. The slight broadening of the $[BCl_4]^-$ resonance may be because of some exchange process at boron, or some hydrogen bonding between $[NMe_3H]$ and $[BCl_4]^-$, although there was no significant sharpening of the line on proton decoupling.

Appendix 3

Chemical Shifts of some Small Molecules

Phosphorus Chemical Shifts

Compound	δP	Coupling Constants	Reference
PH_3	-240	$^1J(P,H)=182Hz$	167,173
PF_2H	(223)	$^1J(P,F)=1140Hz$	167
PF_3	97	$^1J(P,F)=1400Hz$	167,173
$PClF_2$	176	$^1J(P,F)=1390Hz$	167,221
PCl_2F	224	$^1J(P,F)=1320Hz$	167,221
PCl_3	220		167,173
PBr_3	227		167
PI_3	178		167
$[PCl_4]^+$	86		167
PCl_5	-80		167,219
$[PCl_6]^-$	-295		167,219
PF_5	-80	$^1J(P,F)=935Hz$	55,167,173
$[PF_6]^-$	-142	$^1J(P,F)=713Hz$	167,174
$[PF_5H]^-$	-140	see reference 175	55
$PClF_4$		$^1J(P,F)=1000Hz$	173
PCl_2F_3	-28	$^1J(P,F)=1050Hz$	219
PCl_3F_2		$^1J(P,F)=1045Hz$	173
PCl_4F	-46	$^1J(P,F)=1000Hz$	173
PF_3O	-35	$^1J(P,F)=1055Hz$	223
$PClF_2O$	-15	$^1J(P,F)=1140Hz$	173
PCl_2FO	O	$^1J(P,F)=1190Hz$	173
PCl_3O	+2		173
P_4	-461		167
P_4O_6	+113		167,173
$PPhF_4$	-52	$^1J(P,F)=968Hz$	173
$PEtF_4$	-30	$^1J(P,F)=995Hz$	173

$PMeF_4$	-30	$^1J(P,F)=967Hz$	167,173
$PPhCl_4$	-40		222,224
$[PPhCl_3]^+$	96		224
$PEtCl_4$	25		224
$[PEtCl_3]^+$	129		224
PMe_3	-62	$^2J(P,H)=2.7Hz$	167,173
PMe_2H	-99	$^1J(P,H)=200Hz$, $^2J(P,H)=4Hz$	173
PMe_2Cl	+95		173
PMeClO	+65		173
PMe_2HO	+63		173
PEt_3	-20	$^2J(P,H)=14Hz$	167,173
PEt_3O	+48		167,173
PEt_3Cl_2	+110		198
PPh_2H	-41	$^1J(P,H)=220Hz$	173
PPh Cl	+80		173

The above chemical shifts are given in p.p.m. as positive to high frequency of 85% H_3PO_4. Values which we were unable to find, or about which we were uncertain, are marked accordingly.

Fluorine Chemical Shifts

Compound	δF	Coupling Constants	Reference
PF_3	-34	$^1J(P,F)=1400Hz$	167,173
$PClF_2$	-38	$^1J(P,F)=1390Hz$	221,167
PCl_2F	-56	$^1J(P,F)=1320Hz$	221,167
PF_2H	(-116)	$^1J(P,F)=1133Hz$	
PF_3O	-94	$^1J(P,F)=1055Hz$	223
PF_5	-66	$^1J(P,F)= 935Hz$	167,225
$[PF_6]^-$	-71	$^1J(P,F)= 713Hz$	174
PF_4H	-66,-27	see reference	206
$[PF_5H]^-$	-56,-66	see reference	175
BF_3	-131	$^1J(B,F)= 15Hz$	167
$[BF_4]^-$	-151	$^1J(B,F)= 1.4Hz$	167
$[BClF_3]^-$	-125	$^1J(B,F)= 52.2Hz$	167,226
$[BCl_2F_2]^-$	-104	$^1J(B,F)= 54.2Hz$	167,226
$[BCl_3F]^-$	-94	$^1J(B,F)= 79.4Hz$	167,226

The above chemical shifts are given in p.p.m. as positive to high frequency of CCl_3F.

Boron Chemical Shifts.

Compound	δB	Coupling Constants	Reference
BF_3	9.4	$^1J(B,F)=15$ Hz	167
BCl_3	47		167
BBr_3	39		167
BI_3	6		167
$[BF_4]^-$	-1.6,-2.2	$^1J(B,F)= 1.4$Hz	167
$[BClF_3]^-$	1.7	$^1J(B,F)=52.2$Hz	226,167
$[BCl_2F_2]^-$	4.5	$^1J(B,F)=54.2$Hz	226,167
$[BCl_3F]^-$	6.5	$^1J(B,F)=79.4$Hz	226,167
$[BCl_4]^-$	6.7		226,167
$[BBr_4]^-$	-24.1		167
$[BI_4]^-$	-128		167

The above chemical shifts are given in p.p.m. as positive to high frequency of $BF_3(OEt_2)$.

Appendix 4

Published Work

An Iridium Complex of 5-Co-ordinated Phosphorus

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The 5-co-ordinate phosphorus complex $Ir(CO)Cl_2(PEt_3)_2PCl_4$ has been prepared by the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with dichlorine.

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An Iridium Complex of 5-Co-ordinated Phosphorus

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The 5-co-ordinate phosphorus complex $Ir(CO)Cl_2(PEt_3)_2PCl_4$ has been prepared by the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with dichlorine.

Metal complexes of 5-co-ordinated P, As, or Sb are very rare.[1] We have recently prepared[2] the complex $Ir(CO)Cl_2(PEt_3)_2P'Cl_2$ (1) by oxidative addition of PCl_3 to $Ir(CO)Cl(PEt_3)_2$, and it has been characterised by analysis, by mass spectrometry, and by *X*-ray crystallography. The chemical shift† of P′ is 304 p.p.m. Treatment of a solution of (1) in chloroform with dichlorine

† Positive to high frequency of 85% H_3PO_4.

leads to the disappearance of the n.m.r. signals due to (**1**) and to the appearance of new peaks in the P{H} spectrum at +7.6 p.p.m. (t; *J* 17.7 Hz) and −8.6 p.p.m. (d; *J* 17.7 Hz). The product has been isolated as a white powder; analysis for C, H, and Cl is consistent with the formulation of the compound as $Ir(CO)Cl_2(PEt_3)_2PCl_4$ (Cl, found 31.3; calc. 30.4%). The solution in nitromethane is non-conducting, and the n.m.r. spectrum in that solvent is not significantly different from that in dichloromethane. Attempts to obtain the mass spectrum gave molecular ion peaks due to $Ir(CO)Cl_2(PEt_3)_2P(OH)_2Cl_2$ and $Ir(CO)Cl_2(PEt_3)_2POCl_2$, but the analytical data are not consistent with either of these formulations. Treatment of our product with triethylphosphine in dichloromethane gave (**1**) and a compound with a singlet P{H} resonance at 111.9 p.p.m. (found[3] for Et_3PCl_2 112.2 p.p.m.) in essentially quantitative yield; reaction between our product and $Ir(CO)Cl(PEt_3)_2$ gave (**1**) and $Ir(CO)Cl_3(PEt_3)_2$ in high yield. These observations establish the identity of our product (Scheme 1).

$$Ir(CO)Cl_2(PEt_3)_2PCl_2 \quad (\mathbf{1})$$

$$\downarrow Cl_2$$

$$Ir(CO)Cl_2(PEt_3)_2PCl_4 \xrightarrow{Et_3P} (\mathbf{1}) + Et_3PCl_2$$

$$\downarrow Ir(CO)Cl(PEt_3)_2$$

$$(\mathbf{1}) + Ir(CO)Cl_3(PEt_3)_2$$

Scheme 1

The compound appears to hydrolyse very slowly if it is left to stand at room temperature, and it decomposes on sublimation. So far all our attempts to grow single crystals have failed, and so we do not know the stereochemical relationships of the groups round P′ or Ir, except that the Et_3P groups are mutually *trans*.

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An Iridium(III) Complex Containing a PF_4-Group Bound to the Metal

By *E. A. V. Ebsworth**, *John H. Holloway*, *Nicholas J. Pilkington*, and *David W. H. Rankin*

Compounds containing metal atoms bound to pentacoordinated P, As, or Sb atoms are rare[1–3]. We recently[3] described the complex $Ir(CO)Cl_2(PEt_3)_2(P'Cl_4)$ and characterized it by NMR spectroscopy and elemental analysis; however, the characterization of P′ as pentacoordinated was based on the failure of solutions to conduct. By treating **1** with XeF_2, a valuable, mild, fluorinating agent[4], we have now synthesized $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, whose ^{19}F- and ^{31}P-NMR spectra unequivocally show the presence of the $Ir-P'F_4$ group.

$$\underset{\mathbf{1}}{Ir(CO)Cl_2(PEt_3)_2P'F_2} + XeF_2 \xrightarrow[280\ K]{CH_2Cl_2} Xe + \underset{\mathbf{2}}{Cl-Ir(PEt_3)_2(CO)-P'F_4}$$

The reaction is very slow at 220 K but rapid at or above 280 K. The product, which appears to be stable at room temperature in the absence of air or moisture, has been isolated as a white solid and characterized by partial elemental analysis and by NMR spectroscopy. The $^{31}P\{^1H\}$-NMR spectrum in CD_2Cl_2 at 300 K consists of a broad quintet of triplets due to the P′ nucleus (see Fig. 1a) and a narrow doublet of quintets due to the *P* nuclei (see Fig. 1b); the ^{19}F-NMR spectrum at 220 K in the same solvent is a broad doublet of triplets. The $^{31}P\{^{19}F\}$-NMR spectrum is sharp at 220 K, but becomes very broad at 190 K, showing that the molecule is fluxional and that there must be at least two different F sites in the static structure.

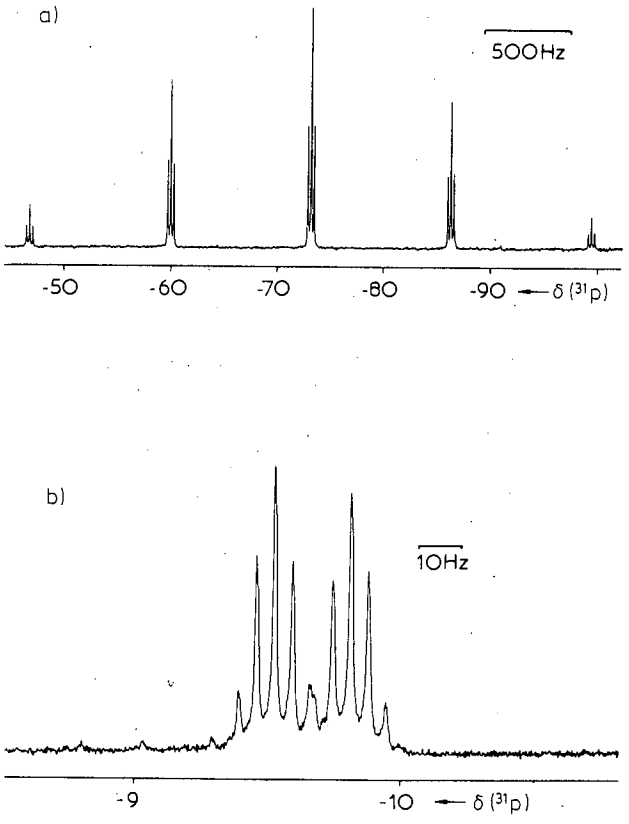

Fig. 1. Part of the 80.1 MHz $^{31}P\{^1H\}$-NMR spectrum of **2** at 300 K in CD_2Cl_2; a) is assigned to the P′ nucleus and b) to the P nuclei.

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[5] **2**, $^{31}P\{^1H\}$- and ^{19}F-NMR (CD_2Cl_2, standard 85% H_3PO_4 for P, CCl_3F for F): $\delta(P) = -9.87$, $\delta(P') = -72.9$, $\delta(F) = -0.20$; $^1J(P'F) = 1062$, $^2J(PP') = 22.6$, $^3J(PF) = 5.8$ Hz.

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Courses Attended

Interpreting the Results of Crystallography

Drs. R.O. Gould, M.D. Walkinshaw and A.J. Welch

Pulse Sequences and their

Applications to n.m.r. Spectroscopy

Dr. G.A. Morris

Inorganic Aspects of Biochemistry

Dr. G.A. Heath

Homogeneous Catalysis

Dr. T.A. Stephenson

Inorganic Cluster Chemistry

Dr. A.J. Welch

Topics in Transition Metal Co-ordination Chemistry

Dr. M. Schröder

Special Seminars; Inorganic Research Group